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Final Report P-4325-I-85-6

DEVELOPMENT OF ANALYTICAL METHODS
FOR THE DETERMINATION OF RESIDUAL
POLYACRYLAMIDE POLYMERS
IN COAL AND OIL PROCESS WATERS

for

Energy, Mines and Resources Canada
CANMET/Coal Research Laboratories
P.O. Bag 1280
Devon, Alberta TOC 1E0

Attention: Dr. W. M. Leung
Scientific Authority

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Work carried out jointly between Guelph Chemical Laboratories (GCL) and
Ontario Research Foundation (ORF) - (Principal Investigator: B. S. Das, Ph.D.)

by

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SUMMARY

This final report presents and discusses the results of CANMET/CRL research contract work on the "Development of Analytical Methods for the Determination of Residual Polyacrylamide Polymers in Coal and Oil Process Waters" (DSS File No. 15SQ.23440-3-9189). The work was conducted jointly by Guelph Chemical Laboratories (GCL) and the Ontario Research Foundation (ORF).

The work program included an initial method development study for the trace analysis of high molecular weight (MW) polyacrylamide (PAM) polymers in water using ultrafiltration (UF) and size exclusion high performance liquid chromatograph (SEHPLC)-UV detection techniques followed by the application of the methodology to the analysis of two process water samples for residual PAM content. The various PAM flocculants studied in the initial method development work included six anionic, one nonionic and one cationic types. The untreated process water samples used for monitoring residual PAM included a coal washery thickener feed sample and a sample of tar sands tailings emulsion. The objective of the study is related to the improvement of the quality of coal, oil and other industrial process waters for reuse or disposal.

During the initial phase of the study, methods have been developed for the separation and analysis of PAM by SEHPLC with highly sensitive UV detection. Two column packings - Gly-CPG (surface modified controlled pore glass) and TSK gel 5000 PW type (hydrophilic polymer gel, MW exclusion limits: 3×10^4 - 8×10^6) were evaluated in SEHPLC work. Methods have also been developed for the isolation of PAM from dilute solutions by membrane ultrafiltration concentration/fractionation technique. The retention times, peak area and peak height of the PAM were found to be reproducible in TSK gel SEHPLC-UV and the response was found linear over a wide concentration range. In addition, very low PAM method sensitivity in the sub-ppm levels was achieved in TSK gel SEHPLC-UV work.

As part of the methods development studies, efficiencies of the protocol procedures (ultrafiltration and SEHPLC analysis) were tested by PAM spiking and recovery studies. Spiking experiments were carried out on both water used as method blank (no sample matrix) and control blanks (coal washery process water free from suspended fines) at different PAM levels to check recoveries and accuracy of the analysis.

The methodology has been applied to the analysis of process water samples. In order to carry out the application studies, the samples were first flocculated with increasing dosages of an anionic PAM and the supernatants analyzed for residual flocculants. The results have demonstrated the applicability of the method to the analysis of residual flocculants in coal process water. Results of another case study with oil process water indicate that residual PAM levels range from not detectable to low ppm at extremely high PAM flocculation dosages. In order to assess the methodology, further studies on residual polyacrylamide determination in various treated industrial waste water, e.g. mineral processing plant effluent, oil refinery wastes and coal washery waters should be undertaken.

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DEVELOPMENT OF ANALYTICAL METHODS FOR THE DETERMINATION
OF RESIDUAL POLYACRYLAMIDE POLYMERS IN COAL AND OIL PROCESS WATERS

1. INTRODUCTION

This report on the above analytical method development study is submitted to DSS Consignee, the Department of Energy, Mines and Resources, CANMET, Coal Research Laboratories, Devon, Alberta. The work was carried out jointly by the Guelph Chemical Laboratories (GCL) and the Ontario Research Foundation (ORF), with ORF acting as subcontractor for GCL.

The objective of this method development and application study for residual polyacrylamide (PAM) is related to the improvement of the quality of coal and oil process waters for reuse or disposal. Tailings from coal washery and heavy oil/bitumen processing plants are often discharged to thickeners and then to tailing ponds. In order to achieve sufficient clarity of the water from the settling ponds for either subsequent reuse or discharge to streams, flocculants such as polyacrylamides are usually added as settling aids.^{1,2,3,4} Because of environmental constraints, e.g. water conservation, limited land for disposal and general stream pollution, the major portions of process water requirements are now reclaimed from tailings thickeners/tailing ponds. Residual flocculants in the reclaimed waters could affect processing operations, e.g. flotation of coal fines. Therefore, there is a need to develop an analytical technique for monitoring traces of residual flocculant in these reclaimed waters. In addition, monitoring the treated effluent for residual PAM is also necessary prior to discharge into streams.

There is very little published literature available on the analysis of trace quantities of PAM in coal and oil process waters. Qualitative determination is normally achieved by adding a non-solvent to precipitate the polymer and observing the appearance of a haze. The quantitative determination of polymer is determined in a similar manner except that an instrument is used to measure the turbidity. For example, Vreugde and Poling⁵ have determined extremely low residual PAM concentration in supernatant water by making use of the principle that polyanions react with fatty cations or cationic poly-electrolytes to produce insoluble complexes, and then measuring the resultant turbidities by light scattering technique. The formation and measurement of precipitates in the above turbidometric procedure are influenced by a number of variables which usually have an effect on the particle size or the solubility of the polymer. The molecular weight distribution of the polymer, the rate of addition of precipitant, the order and the time of mixing, and the presence of residual dissolved organics in process waters are known to cause variation in the measured turbidity. It is, therefore, considered necessary to develop a method to measure residual PAM which is not subject to so many variables.

A spectrophotometric method for the determination of PAM in water has been described by the Dow Chemical Company in a technical bulletin.⁶ The method is based on bromination of amide groups of the PAM to N-bromo amide, which is then used to convert iodide to tri-iodide. The tri-iodide is measured spectrophotometrically at 287 nm. The resulting absorbance can be related to PAM concentration. However, the method is expected to show interferences from other amides, e.g. proteinous material or materials absorbing in the vicinity of 287 nm, e.g. lignin, humic/fulvic acids, phenolic compounds present in process waters.

The techniques of size exclusion high performance liquid chromatography (SEHPLC) or gel permeation chromatography (GPC), as commonly known, together with the sensitive and selective UV detection may be an effective tool for the separation and analysis of PAM. SEHPLC which separates

molecules by their size generally has been used to determine molecular weights (MW) and molecular weight distribution (MWD) of polymers. A new TSK gel-PW type column packing prepared from semi-rigid porous particles of a hydrophilic polymer gel containing the group $-\text{CH}_2-\text{CHOH}-\text{CH}_2\text{O}-$ as the main constituent component, is now available from Toy Soda Manufacturing in Japan. PAM and other water soluble polymers have been analyzed for MW and MWD in aqueous SEHPLC/refractive index (RI) detection system using this new type of packing with no evidence of adsorption.⁷ Recently, the use of another aqueous SEHPLC/RI detection technique using GLY-CPG (Electro Nucleonics) as the column packing and 0.1 M NH_4NO_3 as the mobile phase has been reported for the determination of soluble PAM in aqueous acrylamide monomer.⁸ However, applications of the above packings as well as the use of UV detection in the SEHPLC analysis of residual PAM in process waters have not been reported.

Since the method of detection in SEHPLC may lack the necessary sensitivity in direct determination of trace PAM in process waters, a concentration procedure capable of dealing with large sample volume is necessary. Also necessary is the cleanup/fractionation of the concentrated extract for interference-free PAM analysis. The use of semi-permeable membrane technology (based on separation according to molecular size), e.g. ultra-filtration (UF), for the concentration of a variety of trace organic solutes has been reported for the purification of secondary effluents and for recovery of organics in treated waste water as well as raw and finished water.^{9, 10} A UF technique for concentrating high MW flocculant/polyelectrolyte from dilute aqueous solution has also been reported.¹¹ The main advantage of this method is that the organics in the sample are not likely to be decomposed or otherwise changed during the concentration process. UF may very well be a good concentration/fractionation technique for recovery of high MW PAM in the UF retentate from process waters, provided a suitably high concentration factor can be achieved.

This work under the CANMET/CRL research contract program included an initial method development study for the trace analysis of PAM flocculants in water using the combined UF concentration/fractionation and SEHPLC-RI/UV detection techniques followed by the application of the methodology for the analysis of residual PAM in the flocculation of coal and oil process waters. The various PAM flocculants studied in the initial method development work included six (6) anionic, one (1) nonionic and one (1) cationic types. The untreated process water samples used for monitoring residual PAM included a thickener feed sample from one coal washery and a bitumen-water-suspended fines O/W (oil/water) emulsion tar sands tailings sample. In order to test the applicability of the UF/SEHPLC methodology, the samples were first flocculated with increasing dosage of an anionic PAM (Separan MG 700), and the supernatants analyzed for residual flocculants. The results of the above studies are described in this report.

2. EXPERIMENTAL SECTION

2.1 Preparation of PAM Standards

The three types of PAM used as reference standards are shown in Table 1 (see PAM structures in Figure 1) and were purchased from commercial sources. Some PAMs, namely, Praestol 114, Praestol 2935 and Praestol 2838, were obtained from the stock of the Coal Research Laboratory (CRL), CANMET, Devon, Alberta. Stock solutions of the standards were prepared by dissolving in water at about 100 ppm concentration. Appropriate dilutions with either 0.05 M Na_2SO_4 , 0.05 M NaCl or with water were made to obtain the workable concentration of the standards prior to spiking, flocculation and chromatographic analysis.

2.2 Size Exclusion High Performance Liquid Chromatography (SEHPLC)

2.2.1 Gly-CPG SEHPLC

The glyceryl-controlled pore glass, Gly-CPG packings (37-44 μm , 100 A) obtained from Electro Nucleonics, Inc., were dry packed to prepare four 25 cm x 4.6 mm i.d. columns, and two 100 cm x 4.6 mm i.d. columns for use in series. The columns were prepared as follows: A known quantity of Gly-CPG packings were measured out and poured into a funnel at the top of the column. The column was vibrated until no change in bed volume was observed. A small piece of glass wool was placed at the top of the column. A vacuum line was attached to the top of the column, while the bottom of the column was attached to a stopcock placed in a beaker containing distilled water. The vacuum was applied to the column with the stopcock open allowing the water to slowly fill the column. When the packings were filled with water, the glass wool at the top of the column was removed and the column was ready for use.

The prepared Gly-CPG columns were used in a Beckman Model 112 HPLC with water as the mobile phase at either 2 mL or 3 mL/minute flow rate. A 250 μL loop was used as the injection volume. Either a Waters Associates Model R 401 RI detector or a Beckman Model 165 UV detector was used as detector and a Spectra-Physics SP 4100 was used for data handling. Gly-CPG SEHPLC conditions are shown in Table 2 and the chromatograms of PAM are shown in Figure 2.

2.2.2 TSK Gel 5000 PW SEHPLC

A TSK gel 5000 PW prepacked column (7.5 mm x 30 cm; 17 μm , MW fractionation range: $3 \times 10^4 - 8 \times 10^6$) supplied by Beckman Instruments with a TSK gel 2000 PW precolumn (7.5 mm x 10 cm) supplied by Beckman/Varian Instruments was used in a Beckman Model 112 HPLC with either 0.05 NaCl or 0.05 M Na_2SO_4 as the mobile phase. Flow rate used was either 0.5 mL/min (0.05 M NaCl) or 0.75 mL/min (0.05 M Na_2SO_4). A 250 μL loop was used as the

injection volume. Either a Beckman Model 165, a Varian Varichrom or a Schoeffel Model SF 770 variable wavelength UV detector was used as detector, and a Spectra-Physics SP 4100 was used for data handling. TSK gel SEHPLC conditions are shown in Table 5 and PAM chromatograms are shown in Figure 3.

2.2.3 Identification and Quantitation of Peaks

Peak observed in the sample chromatographic profiles was identified on the basis of retention time and comparison with PAM standard. Peak area method was used for calibration and quantitation of PAM in the samples.

2.3 Ultrafiltration (UF)

An ultrafiltration apparatus (Amicon Model DC-2 hollow fibre dialysis/concentrator, 200-2000 mL capacity) was assembled for concentration/fractionation studies of trace levels of PAM in process water samples. A picture of the Model DC-2 apparatus is shown in Figure 6, and a schematic for concentration using the Model DC-2 is shown in Figure 7. The optimum UF conditions used are as follows:

UF Apparatus	: Amicon Model DC-2
Cartridge Type	: Draflo Hollow Fibre, H 1 P 100-20 (Nominal MW cut-off 100,000)
Flow Rate	: 110 mL/min
Pressure	: 20 psig
Temperature	: Ambient
Concentration Factor	: 10-100

2.4 Process Samples

The two process water samples selected for the study are identified as follows:

- 1) An untreated coal washery thickener feed sample from Telkwa coal plant/Crows Nest Resources Ltd., Alberta. This sample was provided by the Project Scientific Authority. It was analyzed for:

pH	: 6.0
% Suspended Solids	: 1.10
% Total Solids	: 1.34

- 2) An untreated sample of tar sands tailings composed of bitumen-water-suspended fines O/W emulsion. This sample identified as Cell Tails Sand and supplied by Suncor Inc., Oil Sands Group was characterized for the following parameters: % settleable solids, % suspended fines and % bitumen. The sample (pH 7.7) was analyzed as follows:

% Settleable Solids: 100 g sample was first centrifuged at 3500 rpm for 50 minutes, and the supernatant (emulsion) was removed by decantation. The residue was washed with water on the centrifuge, and the water washing added to the supernatant. The washed residue was then dried in an oven set at 100°C to constant weight (~ 15 hours). Found: Settleable Solids: 10.50%.

% Bitumen/Oil: The combined supernatant and washing (~ 175 mL) from the above settleable solids determination were transferred into a separatory funnel, and the emulsion extracted first with n-pentane (2 x 50 mL) and then with benzene (2 x 50 mL). The pentane and benzene extracts were combined, and the solvents removed first in a rotary evaporator under reduced pressure at 30°C and then in a stream of nitrogen for final

drying. Found: Bitumen/Oil (in the emulsion free from settleable solids): 0.42%.

% Suspended Solids: The aqueous phase containing the suspended solids from the above bitumen/oil determination were transferred in a beaker, and the contents in the beaker dried in an oven at 100°C to constant weight (~ 16 hours). Found: Suspended fines: 0.88%.

2.5 PAM Spiking and Recovery Studies

Spiking and recovery studies were performed with both raw and distilled water, and with a coal washery thickener feed filtrate sample. The types and levels of PAM used for spiking are as follows (see Table 7): Separan MG 700 at 0.1, 0.5, 1.0, 5.0, 10.0 ppm; Percol E-10 at 0.5 and 5.0 ppm and Superfloc 127 at 0.1 ppm levels for spiking organic free distilled water (70 ppb TOC); Separan MG 700 at 0.1 ppm levels for spiking raw water (humic acids containing highly coloured water from the Grand River, Brantford), and Separan MG 700 at 2.5 and 5.0 ppm levels for spiking Telkwa coal washery thickener feed filtrate. Prior to spiking, all water samples were filtered using Whatman glass fibre filter (934-AH).

The procedures used for spiking studies with raw and distilled water are as follows: A measured quantity of water sample was spiked with a known volume of 100 ppm PAM standard stock solution in water, and the mixture shaken vigorously. The solution was then fractionated by ultrafiltration following conditions given in Section 2.3. Two different procedures were used for UF work. In one procedure, the fractionation was performed by single pass ultrafiltration and about 100 mL retentate fraction (high MW organic fraction) was collected from either 0.5 L, 1 L or 10 L samples. The retentate was then evaporated to dryness in a rotary evaporator at 30°C under reduced pressure, and the dried residue dissolved in a known small volume of 0.05 M Na₂SO₄ (TSK gel SEHPLC mobile phase), filtered using Millex-SR (0.5 µm, Millipore

Corporation) and the clear filtrate analyzed by SEHPLC. PAM recoveries in the permeates of some samples were also determined. For such determination, the 900 mL permeate from 1 L sample was evaporated to dryness at 30°C under reduced pressure, and the residue dissolved in 0.05 M Na_2SO_4 and analyzed. In another variation, a 2 pass and 3 water wash cycle was given during the UF concentration/fractionation step. In this procedure, a 200 mL (2 x 100 mL) retentate fraction was isolated from a spiked 1 L water or washery filtrate sample by a 2 pass UF (100 mL retentate fraction collected from a 1 L sample by first pass; to the 900 mL permeate fraction, added 100 mL distilled water and from the total 1000 mL, collected another 100 mL retentate fraction by a second pass). To the above 200 mL combined retentate, added 800 mL distilled water, subjected the total 1 L to UF (first wash) and collected 100 mL retentate. Another 2 wash of the 100 mL retentate with distilled water (2 x 900 mL) was given. The final 100 mL retentate isolated by the above 2 pass and 3 wash cycle UF procedures was then evaporated to dryness at 30°C under reduced pressure in a rotary evaporator. The dried residue was dissolved in a known small volume of 0.05 M Na_2SO_4 , filtered using Millex-SR (0.5 μm) and the clear filtrate analyzed for PAM by TSK gel SEHPLC-UV technique.

For spiking and recovery studies with the coal washery filtrate, the thickener feed sample was first allowed to stand for six hours, and the cloudy supernatant decanted and filtered using Whatman 541 filter paper. This filtrate (slightly cloudy) was then spiked with Separan MG 700 at 2.5 and 5.0 ppm levels, shaken by end to end inversion 20 times, allowed to stand overnight (the supernatant still slightly cloudy), and the suspension was then filtered using Whatman glass fibre filter (934-AH). The clear filtrate was then subjected to either single pass or 2 pass/3 wash UF cycles following procedures described above.

2.6 Flocculation and Analysis of Residual PAM in Process Water

Flocculation studies of the process water samples with incremental addition of the anionic Separan MG 700 and analysis of the residual PAM flocculant by UF and SEHPLC techniques were performed as follows:

2.6.1 Coal Washery Thickener Feed

Two sets of flocculation experiments were performed. In one set, nine flocculation experiments at 0.2, 0.4, 1.0, 1.23, 2.44, 3.85, 4.76, 5.66 and 7.41 ppm dosage of Separan MG 700 per litre of suspension were performed, and the supernatants of each flocculation experiment were fractionated by a single pass UF and the retentate fractions analyzed by TSK gel SEHPLC for residual PAM. In the second set of experiments, six flocculation studies were carried out at 1.02, 2.41, 4.90, 6.73, 9.17 and 11.26 ppm PAM dosage, and the supernatants of each flocculation experiment were then fractionated by the 2 pass/3 wash UF, and the retentate fractions analyzed. A typical procedure used was as follows: To either a 500 mL or a 1 L thickener feed suspension (pH 6.0) taken in a 1 L stoppered graduated cylinder, added a known volume of Separan MG 700 dropwise within 1-2 minutes from a 100 ppm stock solution, and the suspension shaken by end to end inversion 20 times, allowed to stand for one hour and the sludge volume recorded. The supernatants (after decantation) and the sludges were then separately filtered using Whatman glass fibre filter (934-AH), and the filtrates combined. The clear filtrate was then fractionated either by single pass or by 2 pass/3 wash UF cycles as described in Section 2.5, and the fractions analyzed for residual PAM. The flocculation and UF conditions are given in Tables 8-9.

2.6.2 Tar Sands Tailings Emulsion

A series of flocculation experiments with incremental addition of anionic Separan MG 700 PAM at 23.0, 28.5, 31.0 and 33.3 ppm dosage were carried out with the Suncor tar sands tailings sample. Procedures used in carrying out the flocculation studies are as follows:

About 300 mL tailings were first centrifuged at 3500 rpm for 40 minutes to remove the settleable solids. A 250 mL aliquot of the supernatant (emulsion) was decanted in a 500 mL beaker, the pH adjusted to 5.0 from 7.7 with 42.5 mL of 0.1 N H_2SO_4 , and the emulsion flocculated with known volume of Separan MG 700 added from 100 ppm stock solution. A Bird-Phipps flocculator stirring at 100 rpm for six minutes (1 minute for flocculant addition and 5 minutes for flocculation) was used for all flocculation experiments. After six minutes, the contents of the beaker were transferred into a 500 mL graduated cylinder using a distilled water rinse (~ 200 to 300 mL) and were then allowed to settle. The emulsion separated into two phases - an aqueous clear top layer and a sludge layer at the bottom. A photograph showing the flocculations of the emulsion at different flocculant dosages at 1 hour settling time is shown in Figure 12. The sludge volumes were recorded at various time intervals. The aqueous layer is separated, concentrated by a 1 pass/2 wash UF technique, and the UF retentate fraction analyzed for residual PAM. The flocculation and UF conditions are presented in Tables 10-11.

3. RESULTS & DISCUSSIONS

3.1 Development of Analytical Methods

The initial phase of the program involved development of suitable methods for the trace analysis of PAM in process waters based on size exclusion high performance liquid chromatography (SEHPLC)-RI/UV detection techniques.

3.1.1 SEHPLC Analysis

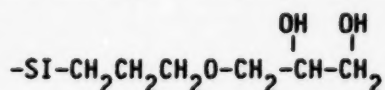
For methods development, all three types of polyacrylamide (PAM) flocculants - anionic, nonionic and cationic which have found widespread use

in flocculation of suspended fines in coal and other industrial process waters were selected as reference for analysis by the SEHPLC method. The various PAMs studied are listed in Table 1 and the typical structure of the three types of PAM are presented in Figure 1.

SEHPLC is a liquid chromatographic technique which separates molecules according to their sizes. This technique is generally used to determine the MW and MWD of polymers. Separation is accomplished by repeated exchange of the sample molecules between the mobile bulk solvent and the stagnant solvent within the pores of the column packing. Thus, the pore size of the column packing particles determines the range of molecular size which can be separated. Sample molecules with the largest size (highest MW) elute out from the column first followed by the smaller molecules. Two important elution limits are defined for every column and are called total exclusion and total permeation limits. Sample molecules which are too large to access any of the column packing pores elute from the column at the total exclusion limits, and small molecules small enough to access all volumes elute at the total permeation limits. Between these two limits is the separation range of the column. This method of SEHPLC analysis can, therefore, determine molecular species ranging from low MW to high MW.

The use of various semi-rigid and rigid column packings in aqueous SEHPLC systems for the analysis of high molecular weight compounds has been described in the literature. In the present study, two column packings were evaluated for the trace analysis of high molecular weight PAM polymeric flocculant in water by SEHPLC. They are as follows:

- 1) Rigid packings [Gly-CPG ... glyceryl-controlled pore glass, 37-44 μm particles of 170A pore size containing a covalently bonded hydrophilic nonionic carbohydrate monolayer,



(from Electro Nucleonics Inc., Fairfield, N.J., U.S.A.)).

- 2) Semi-rigid packings [TSK gel type PW, 15 μ m diameter particles of hydrophilic polymer gel containing the group $-\text{CH}_2\text{CHOH}-\text{CH}_2\text{O}-$ as the main constituent component (from Toyo Soda Manufacturing Co. Ltd., Japan)].

The purpose of covering the active sites on the surface of the above glass and polymer gel packings with hydrophilic groups is to prevent or minimize adsorption of the solutes during SEHPLC analysis.

Refractive index (RI) detector is most commonly used as the method of detection in the SEHPLC analysis of polymers. However, it may lack adequate sensitivity in trace PAM analysis. Use of reverse phase HPLC technique using a low wavelength UV detection at 208 nm in the determination of trace acrylamide monomer in polyacrylamide and in environmental samples has been reported by Skelly and Hussar.¹² UV detection in this study allowed measurement of acrylamide with high sensitivity. In the present study, a similar low wavelength UV detection was evaluated in the PAM analysis for improved sensitivity.

3.1.1.1 Gly-CPG SEHPLC Analysis

The Gly-CPG controlled pore glass packings were evaluated for the analysis of PAM following procedures of Chow and Jewett⁸ who reported the use of this packing in aqueous SEHPLC/RI analysis of PAM in acrylamide monomer solution. In our study, three different column configurations - 1) 4 x 25 cm x 4.6 mm i.d. columns in series, 2) 1 x 100 cm x 4.6 mm i.d. column and 3) 2 x 100 cm x 4.6 mm i.d. columns in series. Water was used as the eluent instead of 0.1 N NH_4NO_3 used by Chow and Jewett⁸ because of interferences from NH_4NO_3 in UV detection. Other mobile phases evaluated for the separation of PAM in this work include aqueous NaCl of 0.025 M, 0.05 M and 0.2 M concentration. Other chromatographic conditions are shown in Table 2.

The SEHPLC chromatograms of the three PAM - the anionic Separan MG 700, nonionic Superfloc 127 and cationic Percol 352, each run at about 10 ppm concentration in both RI and UV detection mode are shown in Figure 2. The data on precision and reproducibility studies performed on 1 x 100 cm and 2 x 100 cm columns with Separan MG 700 and Superfloc 127 are shown in Table 3. The study has indicated the following:

- The Gly-CPG SEHPLC method gives good resolution of PAM and allows analysis of the three types of PAM in both RI and UV detection using water as the mobile phase.
- The RI detection fails to provide adequate sensitivity. Limits of detection achievable by this method of detection are calculated to be between 10-15 ppm for the three PAM.
- The UV detection @ 208 nm gives much higher sensitivity than RI detection. Minimum detection limits of PAM achievable by UV detection are in the 1-2 ppm range.
- The precision of the method studied by multiple injection gives good reproducibility in retention times, peak areas and peak heights of each of the three PAM. However, the column life is found to deteriorate with continued usage resulting in poor resolution.
- Studies of the effect of strong electrolyte on the retention characteristics of the Separan MG 700 in Gly-CPG SEHPLC in aqueous NaCl mobile phase of various ionic strengths show poor base line and fail to show the typical PAM peak observed with water used as the mobile phase.

3.1.1.2 TSK Gel 5000 PW SEHPLC

A TSK gel 5000 PW type column with MW fractionation range of $3 \times 10^4 - 8 \times 10^6$ was evaluated for the separation of the PAM by SEHPLC-UV detection. This column was chosen over other PW types because of its selectivity in resolving PAM of MW greater than 10^5 . Initial studies with water as the mobile phase have shown that the PAM is strongly adsorbed on the TSK gel and the adsorption increases with each successive injection of PAM (see Table 4). This suggests that even with the surface modified TSK gel packings, it is necessary to add an active site inhibitor, e.g. salt to the water mobile phase to prevent or minimize PAM adsorption effects. Addition of salt of proper ionic strength may also be necessary to overcome the polyelectrolyte or ion exchange effects for reproducible analysis of the PAM polymer. The effect of addition of strong electrolyte, e.g. NaCl, Na_2SO_4 of different ionic strengths on the PAM retention on TSK gel packings was therefore studied and the proper SEHPLC mobile phases and flow rates optimized. They are as follows: 0.05 M NaCl @ 0.50 mL/min and 0.05 M Na_2SO_4 @ 0.75 mL/min. Other chromatographic conditions are presented in Table 5.

The TSK gel SEHPLC/UV chromatograms of two anionic - Separan MG 700 and Hercofloc 1021, one nonionic Superfloc 127 and one cationic Percol 352 PAM, each run at about 10 ppm concentration using 0.05 M NaCl at 0.50 mL/min flow rate are shown in Figure 3. Chromatograms of analysis of four anionic PAM at about 10 ppm concentration, namely, Separan MG 700, Praestol 114 (50% charge), Praestol 2935 (35.4% charge) and Praestol 2830 (12.5% charge) in 0.05 M Na_2SO_4 at 0.75 mL/min flow rate are presented in Figure 4. The precision and reproducibility data from the analysis of Separan MG 700 in 0.05 M Na_2SO_4 at two different concentrations, e.g. 20 and 40 ppm, are shown in Table 6, and a calibration curve for Separan MG 700 run at concentrations ranging between 5 and 100 ppm in the same mobile phase is shown in Figure 5. The study has indicated the following:

- TSK gel SEHPLC using water as the mobile phase shows strong adsorption of PAM. In order to prevent or minimize PAM adsorption, use of aqueous mobile phase containing strong electrolyte, e.g. NaCl, Na_2SO_4 of proper ionic strength is necessary.
- TSK gel SEHPLC/UV detection using either 0.05 M NaCl or 0.05 M Na_2SO_4 mobile phase allows good resolution of anionic and nonionic PAM but fails to resolve the cationic PAM type (0.05 M Na_2SO_4 is preferred over 0.05 M NaCl because of its less corrosive action on HPLC pump components. This mobile phase is also being used in TSK gel SEHPLC analysis of water soluble polymers at CRL).
- The three anionic PAM Praestol samples of similar concentrations when analyzed by TSK gel SEHPLC gives similar retention times but different peak areas. The retention volumes seem to increase with decreased charge density, e.g. Praestol 2830 with an anionic charge of 12.5% gives the largest peak area (e.g. 40682 units), whereas the same PAM with 50% anionic charge shows the lowest peak area (e.g. 20429 units) (see Figure 4).
- The precision data show excellent reproducibility in retention times, but fail to indicate good reproducibility in peak areas. This problem of achieving highly reproducible peak areas is probably due to adsorption and ion exchange of the PAM on the hydrophilic TSK gel SEHPLC supports. The relative precision of the analytical method was found to be about $\pm 20\%$ at the 95% confidence level in the concentration range of 20-40 ppm. This implies that at the above level of precision, an average value, for example, 0.4 ppm residual PAM in effluent water will lie between 0.32 and 0.48 ppm when determined by the SEHPLC technique.

- The TSK gel SEHPLC/UV response for the anionic PAM, e.g. Separan MG 700 is found to be linear at concentrations studied which ranged from 5 and 100 ppm.
- The limits of detection of the PAM analyzed by TSK gel SEHPLC/UV detection is between 1 - 2.5 μg . This represents the amount of standard PAM material to give a response height of 1 - 2 cm which is roughly twice the background noise. The actual method sensitivity in the analysis of PAM in process water would, however, depend on the amount of sample material injected, the background noise (interferences) and the recovery throughout the method. Thus, for example, assuming 100% recovery during UF and other sample preparation steps, a 250 μL injection of the PAM extract from a 1 L process water sample concentrated to 5 mL retentate fraction will give method sensitivity of the PAM to lie around 0.02 - 0.05 ppm.

3.2 Application of Analytical Methods

The analytical methods developed in the initial phase of the program were applied to the analysis of residual PAM in two process water samples.

3.2.1 Spiking and Recovery Studies

Sample preparation procedures used for concentration and fractionation/cleanup of the dilute supernatant originating from flocculation of process water were based on membrane ultrafiltration technique. Initially, the efficiencies of the protocol procedures (ultrafiltration and SEHPLC analysis) were tested by PAM spiking and recovery studies. Recovery studies were made by spiking both water used as method blank (no sample matrix) and control blank (coal washery process water free of suspended fines and with minimum or no background) at different levels of PAM to determine the recoveries for the PAM through the various procedural steps.

Method blank for the methods validation studies consisted of:

1) organic free distilled water (TOC 70 ppb) and 2) Brantford river raw water (highly coloured due to the presence of humic/fulvic acids). The PAM and their levels used for spiking are as follows: 1) Distilled water sample at 0.1, 0.5, 1.0, 5.0 and 10 ppm of Separan MG 700, 0.5 and 5 ppm of Percol E-10 and 0.1 ppm of Superfloc 127 and 2) Raw water sample at 0.1 ppm of Separan MG 700.

Control blank for the methods validation studies consisted of Telkwa coal washery thickener feed filtrate (free from suspended fines). It was spiked with Separan MG 700 at 2.5 and 5 ppm levels.

Initially, the control blanks were subjected to either single pass or 2 pass/3 wash UF (see Experimental) and the retentate fraction (2.5 mL from 500 mL washery thickener feed filtrate) analyzed by TSK gel SEHPLC/UV to determine the background levels. No background (interferences) was observed in the thickener feed filtrate (see Figure 9).

The results of spiking and recovery studies of the raw and distilled waters and of the thickener feed filtrate are shown in Table 7. Spiking studies of the raw and distilled water gave high PAM recoveries in the retentate fraction ranging from 88-100% when the concentration/fractionation was achieved by single pass ultrafiltration. (Chromatograms of 0.5 ppm Separan MG 700 and Percol E-10 spiked distilled water retentate and the corresponding PAM standards are shown in Figure 8). However, when the spiked distilled water samples were processed by a 2 pass/3 wash UF cycles (this step was necessary to prevent or minimize the accumulation of process water salt in the retentate fraction), the spiking studies at three levels, e.g. 1, 5 and 10 ppm gave an average recovery of 75.5% PAM, indicating about 24.5% of the flocculant is lost during the UF wash cycles.

Spiking and recovery studies with the Telkwa coal washery thickener feed filtrate gave PAM recoveries in the retentate fractions of only 30 and 35.2% respectively, at the 2.5 and 5 ppm levels of spiking from a single pass ultrafiltration. (Two chromatograms of 5.0 ppm Separan MG 700 spiked thickener feed filtrate retentate and permeate are shown in Figure 9). In contrast, a 2 pass/3 wash UF processing gave 50% PAM recovery from the 2.5 ppm spiking experiment. It is likely that of the 50% loss of polyacrylamide in the above experiment, about 25.5% is lost due to the interactions of the flocculant with the soluble impurities in the thickener feed filtrate, and the remaining 24.5% is lost during the 2 pass/3 wash UF cycles observed in distilled water spiking studies.

It is to be noted that the single pass ultrafiltration of the washery thickener feed filtrate produced a retentate fraction which contained a voluminous precipitate of salt. (This precipitate was filtered using Millex-SR, 0.5 μ m prior to analysis of the retentate by SEHPLC). It is likely that some polyacrylamide is lost in the precipitate by absorption/entrainment. To avoid this loss, desalting of the retentate fraction was performed by giving several distilled water wash in the 2 pass/3 wash UF mode. However, the above desalting step also resulted in some loss of the polyacrylamide (~ 24.5%) in the permeate during the wash cycle.

3.2.2 Flocculation and Analysis of Process Water Samples

3.2.2.1 Coal Process Water

In order to test the applicability of the UF/TSK gel SEHPLC technique, a series of flocculation experiments with incremental addition of Separan MG 700 were carried out with a washery thickener feed sample from Telkwa coal plant, and both UF retentate and permeate fractions of supernatants of each flocculation experiment analyzed for residual flocculant.

Two sets of flocculation and UF experiments were performed (see Experimental, Section 2.6.1). In the first set of experiments, the washery effluent was flocculated with 0.2, 0.4, 1.0, 1.23, 2.44, 3.85, 4.76, 5.66 and 7.41 ppm dosage of Separan MG 700 per litre of suspension, and the supernatants processed by a single pass UF. The results of the flocculation and analysis of residual flocculant of the above set of experiments are presented in Table 8 (see Figure 10 for retentate and permeate chromatographic profiles of the 2.44 and 7.41 ppm flocculation experiments). As can be seen from the table, the residual PAM (~ 0.20 ppm) is only observed in the UF retentate of the thickener feed sample flocculated at 7.41 ppm PAM dosage, even though good flocculation/clarification is found to occur at a much lower dosage at around 1.0 ppm.

In the second set of experiments, the washery effluent was flocculated with 1.02, 2.41, 4.90, 6.73, 9.17 and 11.26 ppm dosage of Separan MG 700 per litre of suspension, and the supernatants subjected to a 2 pass UF fractionation/concentration step to isolate first a retentate fraction which was then desalted by a 3 water wash cycle in UF. The results of flocculation and analysis of residual flocculant from the above set of experiments are given in Table 9. Quantitation was performed using both 30 ppm and 100 ppm Separan MG 700 as external calibration standards, and the average of the two quantitations was taken as the residual flocculant concentration. Previous studies with distilled water spiked at 1, 5 and 10 ppm levels had shown an average 25% loss of flocculant during the 2 pass/3 wash cycles UF concentration/desalting steps (see Table 7). Since a similar loss is likely to occur in the flocculation/UF studies with coal washery effluent, a correction for this loss is given to the observed residual flocculant concentration. This is shown in Table 9.

The variation of the residual flocculant concentration with increasing flocculant concentration is shown in a curve presented in Figure 11. The data are from the 2 pass/3 wash cycles UF experiment. As expected, an increase in residual concentration is observed with an increase in

flocculant dosage. This demonstrates the applicability of the UF/SEHPLC technique in the analysis of residual PAM flocculant in coal process waters.

3.2.2.2 Oil Process Water

In order to test the applicability of the UF/SEHPLC technique, a series of flocculation experiments with incremental addition of Separan MG 700 at 23, 28.5, 31.0 and 33.3 ppm levels were carried out with a Suncor tar sands tailings (oil-water-clay fines emulsion) sample, and the supernatants of each flocculation experiment were processed by a 1 pass/2 wash cycles UF, and the retentate fraction analyzed for residual flocculant by TSK gel SEHPLC. The flocculation conditions and results are shown in Table 10 and a photograph showing the flocculation of emulsions at different flocculant dosage is given in Figure 12.

The results of analysis of residual flocculants from the above four flocculation experiments are shown in Table 11. The results show extremely low and negligible recoveries of the residual flocculant in the supernatant, even in cases when large excesses were used. Optimum flocculant dosage was found to be around 25 ppm. One explanation for the absence of residual flocculants is their possible loss either by physical absorption (not adsorption) on the oily sludge or by chemical reaction with bitumen asphaltenic/naphthenic acids. In order to test the applicability of the UF/SEHPLC technique in the residual flocculant analysis in flocculated tar sands tailings, flocculation studies using polyacrylamide dosages higher than those used in the present study would be necessary. This is beyond the scope of the project.

4. CONCLUSIONS

Results of the evaluation studies of two SEHPLC column packings indicate that the TSK gel 5000 PW type gel having MW exclusion limits between

$3 \times 10^4 - 8 \times 10^6$ is suitable for the analysis of both anionic and nonionic polyacrylamide in water. This column is chosen over the surface modified controlled pore glass packings because of better resolution and sensitivity and longer column life. The results of the application studies of the combined UF and TSK gel SEHPLC-UV methodology indicate the method is applicable to the analysis of residual polymer in coal process water. Results of another case study with oil process water (tar sands tailings emulsion) indicate that residual polyacrylamide levels range from not detectable to low ppm at extremely high polymer flocculation dosages. Further studies on residual polyacrylamide determination in various treated industrial waste waters, e.g. tailings from mineral processing plants, refinery oily waste water, coal washery effluents, are recommended for validation of the methods developed in the present work.

Development of a spectrophotometric method for residual polyacrylamide determination in water is now under way at Guelph Chemical Laboratories. The results of this work when completed will be sent as an appendix to this report.

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TABLES 1 - 11

TABLE 1

List of Commercial PAM Flocculants Studied

Flocculant	Type	MW/Ionic Charge	Manufacturer
Separan MG 700	Anionic	$10^5 - 5 \times 10^6$	Dow Chemical
Percol E-10	Anionic	High MW	Allied Colloids
Hercofloc 1021	Anionic	High MW	Hercules
Praestol 114	Anionic	50% charge	CRL/Devon, Alberta
Praestol 2935	Anionic	35.4% charge	CRL/Devon, Alberta
Praestol 2830	Anionic	12.5% charge	CRL/Devon, Alberta
Superfloc 127	Nonionic	$> 15 \times 10^6$	Cyanamid
Percol 352	Cationic	$5 \times 10^6 - 15 \times 10^6$	Allied Colloids

TABLE 2

Gly-CPG SEHPLC Conditions

Instrument	: Beckman Model 112 HPLC
Column	: 4 x 25 cm x 4.6 mm Gly-CPG (Electro Nucleonics) 1 x 100 cm x 4.6 mm Gly-CPG 2 x 100 cm x 4.6 mm Gly-CPG
Mobile Phase	: Water
Flow Rate	: 2 mL/min
Pressure	: 0.45 - 0.53 K psi
Temperature	: Ambient
Injection Volume	: 250 μ L
Detector	: Beckman Model 165 variable wavelength UV detector @ 208 nm and Waters Associates Model R 401 RI detector
Data System	: Spectra-Physics SP 4100 Computing Integrator

TABLE 3Gly-CPG SEHPLC Reproducibility Data (a)

Run #	Retention Time (min)	Peak Area (Arbitrary Units)	Peak Height (cm)
<u>1 x 100 cm column</u>			
<u>Separan MG 700 (10.0 ppm)</u>			
1	3.48	35409	8.20
2	3.46	40990	8.40
3	3.41	37220	8.25
<u>Superfloc 127 (10.7 ppm)</u>			
1	3.51	39448	8.60
2	3.49	35388	8.05
3	3.45	40162	8.65
<u>2 x 100 cm columns</u>			
<u>Separan MG 700 (10.0 ppm)</u>			
1	4.60	79888	14.10
2	4.56	82239	14.42
3	4.45	79379	14.39
4	4.56	73340	14.90
5	4.58	76457	15.15

(a) For Chromatographic Conditions see Table 2/UV detection

TABLE 4

Separan MG 700 (10 ppm) Adsorption
in TSK Gel SEHPLC with Water Mobile Phase (a)

Run #	Retention Time (min)	Peak Area (Arbitrary Units)
1	6.33	51391
2	6.30	45490
3	6.24	35826
4	6.23	25882
5	6.22	16283
6	6.25	10495
7	6.24	7740

(a) SEHPLC Conditions same as in Table 5 except water at 1.0 mL/min was used as mobile phase

TABLE 5

TSK Gel SEHPLC Conditions

Instrument	: Beckman Model 112 HPLC
Column	: TSK Gel 5000 PW (7.5 mm x 30 cm; 17 μ m) with TSK Gel PW precolumn (7.5 mm x 10 cm)
Mobile Phase and Flow Rate	: 0.05 M NaCl @ 0.5 mL/min; 0.05 M Na ₂ SO ₄ @ 0.75 mL/min
Injection Volume	: 250 μ L
Temperature	: Ambient
Detector	: Beckman Model 165, Varian Varichrom, Schoeffel Model 770 - Variable Wavelength UV Detector at 208 nm
Data System	: Spectra-Physics SP 4100 Computing Integrator

TABLE 6

Precision/Reproducibility Measurement for 20 and 40 ppm Separan MG 700
by TSK Gel SEHPLC

	20 ppm			40 ppm		
	RT (min)	Area (units)	Concentration from Calibration Curve (ppm)	RT (min)	Area (units)	Concentration from Calibration Curve (ppm)
Day 1						
Injection 1	8.93	25205	21.2	8.86	38192	33.0
Injection 2	8.83	27054	22.6	9.04	40743	35.2
Injection 3	8.96	26012	21.9	9.02	47334	40.9
Injection 4	9.13	29253	24.6	8.93	48519	42.0
Injection 5	9.11	25332	21.3	9.04	39216	33.9
Day 2						
Injection 1	8.91	22415	18.9	8.98	40967	35.4
Injection 2	8.95	28553	24.0	8.98	49766	43.0
Injection 3	8.98	23542	19.6	8.89	49368	42.7
Injection 4	8.95	26090	22.0	9.05	48458	41.9
Injection 5	9.14	24961	21.0	8.96	43410	37.5
Day 3						
Injection 1	8.96	24951	21.0	8.88	40351	34.9
Injection 2	8.88	21265	17.9	8.90	49175	42.5
Injection 3	9.00	25472	21.4	8.97	41835	36.2
Injection 4	9.10	22000	18.5	8.99	40703	35.2
Injection 5	9.08	29489	24.8	8.75	42244	36.5
Day 4						
Injection 1				8.86	40942	35.4
Injection 2				8.89	41444	35.8
Injection 3				8.97	43606	37.7
Injection 4				8.84	40352	34.9
Injection 5				8.91	44310	38.3
Day 5						
Injection 1				9.00	44655	38.6
Injection 2				9.00	41411	35.8
Injection 3				8.93	46149	39.9
Injection 4				9.07	50701	43.8
Injection 5				8.97	50739	43.9
Average			21.4			38.2
Standard Deviation			2.08			3.44
Relative Standard Deviation			10%			9%
Precision (95% Confidence Level)			± 19.4%			± 18.0%

TABLE 7
Polyacrylamide Spiking and Recovery Studies
with Raw and Distilled Water and Telkwa Thickener Feed Filtrate (a)

Experiment No.	Volume of Liquid Spiked (mL)	Volume of 100 ppm Polyacrylamide Added (mL)	Polyacrylamide Added (ppm)	Retentate Volume (mL)	Permeate Volume (mL)	% Recovery
<u>Single Pass Ultrafiltration</u>						
I	10 L Distilled Water	10 mL Separan MG 700	0.1	100	NA ^(b)	> 100
II	10 L Distilled Water	10 mL Superflac 127	0.1	100	NA	> 100
III	10L Brantford Grand River Raw Water	10 mL Separan MG 700	0.1	100	NA	> 100
IV	500 mL Distilled Water	2.5 mL Separan MG 700	0.5	5	NA	> 100
V	500 mL Distilled Water	2.5 mL Percol E-10	0.5	5	NA	> 100
VI	1000 mL Distilled Water	10 mL Separan MG 700	1.0	5	NA	88
VII	500 mL Distilled Water	25 mL Separan MG 700	5.0	100	NA	> 100
VIII	500 mL Distilled Water	25 mL Percol E-10	5.0	50	NA	> 100
IX	500 mL Telkwa Filtrate	12.5 mL Separan MG 700	2.5	15	NA	30
X	500 mL Telkwa Filtrate	25 mL Separan MG 700	5.0	20	20 ^(c)	35.2
<u>2 Pass/3 Wash Ultrafiltration Cycle</u>						
XI	1000 mL Distilled Water	10 mL Separan MG 700	1.0	5	NA	74
XII	1000 mL Distilled Water	50 mL Separan MG 700	5.0	5	NA	78
XIII	1000 mL Distilled Water	100 mL Separan MG 700	10.0	5	NA	80
XIV	1000 mL Telkwa Filtrate	25 mL Separan MG 700	2.5	5	NA	50 ^(d)

(a) TSK Gel SEHPLC Conditions shown in Table 4/Experiment I-III.
Retentate analyzed using 0.05 M NaCl at 0.5 mL/min; Experiment IV-XIV.
Retentate analyzed using 0.05 M Na₂SO₄ at 0.75 mL/min.

(b) NA = not analyzed.

(c) = None detected.

(d) Of polyacrylamide loss of 50%, loss from 3 wash cycle in UF is 24.5% and the remaining 25.5% loss is attributed to the interaction of the flocculant with the soluble impurities in the Telkwa filtrate.

TABLE 8
Analysis of Residual Flocculant in Telkwa Coal Washery Thickener Feed Effluent (a)
by Single Pass UF/TSK Gel SEHPLC-UV Technique

Experiment No.	Volume of Effluent Flocculated (mL)	Volume of 100 ppm Separan MG 700		Sludge Volume after 1 hr. (mL)	Retentate Volume (mL)	Permeate Volume (mL)	Residual Separan MG 700 (b)	
		(mL)	(ppm)				Retentate (ppm)	Permeate (ppm)
I	1000	2	0.2	40	5.0	NA ^(c)	ND ^(d)	NA
II	500	2	0.4	-	2.5	NA	ND	NA
III	500	5	1.0	-	2.5	NA	ND	NA
IV	1000	12.5	1.23	60	5.0	10	ND	ND
V	1000	25	2.44	70	5.0	10	ND	ND
VI	500	20	3.85	-	2.5	NA	ND	NA
VII	500	25	4.76	-	2.5	NA	ND	NA
VIII	1000	60	5.66	70	5	10	ND	ND
IX	1000	80	7.41	72	5	10	0.20	ND

(a) % Solid: 1.34; % Suspended solid: 1.10; pH: 6.0.

(b) TSK Gel SEHPLC Conditions shown in Table 5/0.05 M Na₂SO₄ at 0.75 mL/min was used as the mobile phase.

(c) NA = Not analyzed.

(d) ND = None detected.

(e) - = Not recorded. Allowed to settle for only 15 minutes prior to filtration/UF experiments.

TABLE 9
Analysis of Residual Flocculant in Telkwa Coal Washery Thickener Feed Effluent (a)
by 2 Pass and 3 Wash Cycles UF/TSF Gel SENPLC-UV Technique

Experiment No.	Volume of Effluent Flocculated (mL)	Amount of 102.8 ppm Separan MG 700 Added		Flocculant Added (ppm)	Retentate Volume (mL)	Residual Flocculant Found (b)			Loss of Flocculant in UF Wash Cycle (c) (ppm)	Corrected Residual Flocculant (ppm)
		(mL)	(mg)			Calib. & Quant. using 30 ppm Standard (ppm)	Calib. & Quant. using 100 ppm Standard (ppm)	Average Residuals (ppm)		
I	500	5	0.514	1.02	5	ND ^(d)	ND	0.00	-	0.00
II	500	12	1.23	2.41	5	0.13	0.12	0.125	0.603	0.73
III	500	25	2.57	4.90	5	0.65	0.60	0.625	1.225	1.85
IV	500	35	3.60	6.73	5	1.37	1.26	1.315	1.683	3.00
V	500	49	5.06	9.17	5	2.76	2.54	2.650	2.293	4.95
VI	500	61.5	6.33	11.26	5	4.80	4.41	4.605	2.815	7.42

(a) % Total solids: 1.34; % Suspended solids: 1.10; pH: 6.0

(b) TSK Gel SENPLC Conditions shown in Table 5/0.05 M Na₂SO₄ at 0.75 mL/min was used as the mobile phase.

(c) After correction of 25% loss of flocculant in 2 pass/3 wash UF cycles. This average loss was determined by flocculant spiking and recovery studies in distilled water (see Table 7).

(d) ND = None detected.

TABLE 10

Results of Flocculation of Suncor Tar Sands Tailings Emulsion

Experiment No.	Volume of Emulsion used for Flocculation (mL)	Volume of 100 ppm Separan MG 700 Added (mL)	Separan MG 700 Dosage (ppm)	Total Volume after Flocculation (dilution with water) (mL)	Sludge Volume (mL)		
					1 hr.	5 hrs.	15 hrs.
I	250	75	23.08	450	0.0 (no separation)	437 (sl. cloudy)	405 (clear)
II	250	100	28.57	522	387 (cloudy)	352 (clear)	320 (clear)
III	250	112.5	31.03	510	267 (sl. cloudy)	210 (clear)	177 (clear)
IV	250	125	33.33	512	202 (almost clear)	165 (clear)	145 (clear)

TABLE 11

Analysis of Residual Flocculant
in Suncor Tar Sands Tailings Emulsion (a)
by 1 Pass/2 Wash Cycles UF/TSK Gel SEHPLC Technique

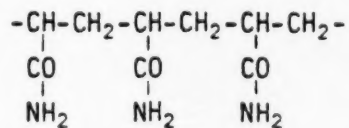
Experiment No.	Volume of Emulsion Flocculated (mL)	Flocculant Added (ppm)	Supernatant Volume after Dilution with Water (mL)	UF Retentate Volume (mL)	Residual Flocculant (b) (ppm)
I	250	23.08	450	2.5	0.16
II	250	28.57	522	2.5	0.16
III	250	31.03	510	2.5	0.39
IV	250	33.33	512	2.5	0.45

(a) pH 7.7; % non-settleable suspended solids 0.88; % oil 0.42.

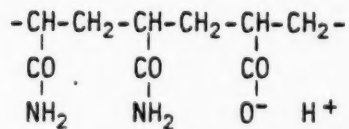
(b) TSK-Gel SEHPLC Conditions shown in Table 5/0.05 M Na_2SO_4 at 0.75 mL/min was used as the mobile phase.

FIGURES 1 - 12

1) Non-ionic PAM (Superfloc 127)



2) Anionic PAM (Separan MG700)



3) Cationic PAM (Percol 352)

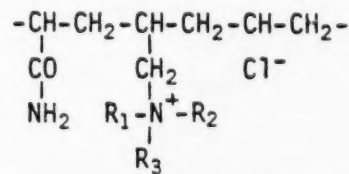


FIGURE 1

PAM Structures

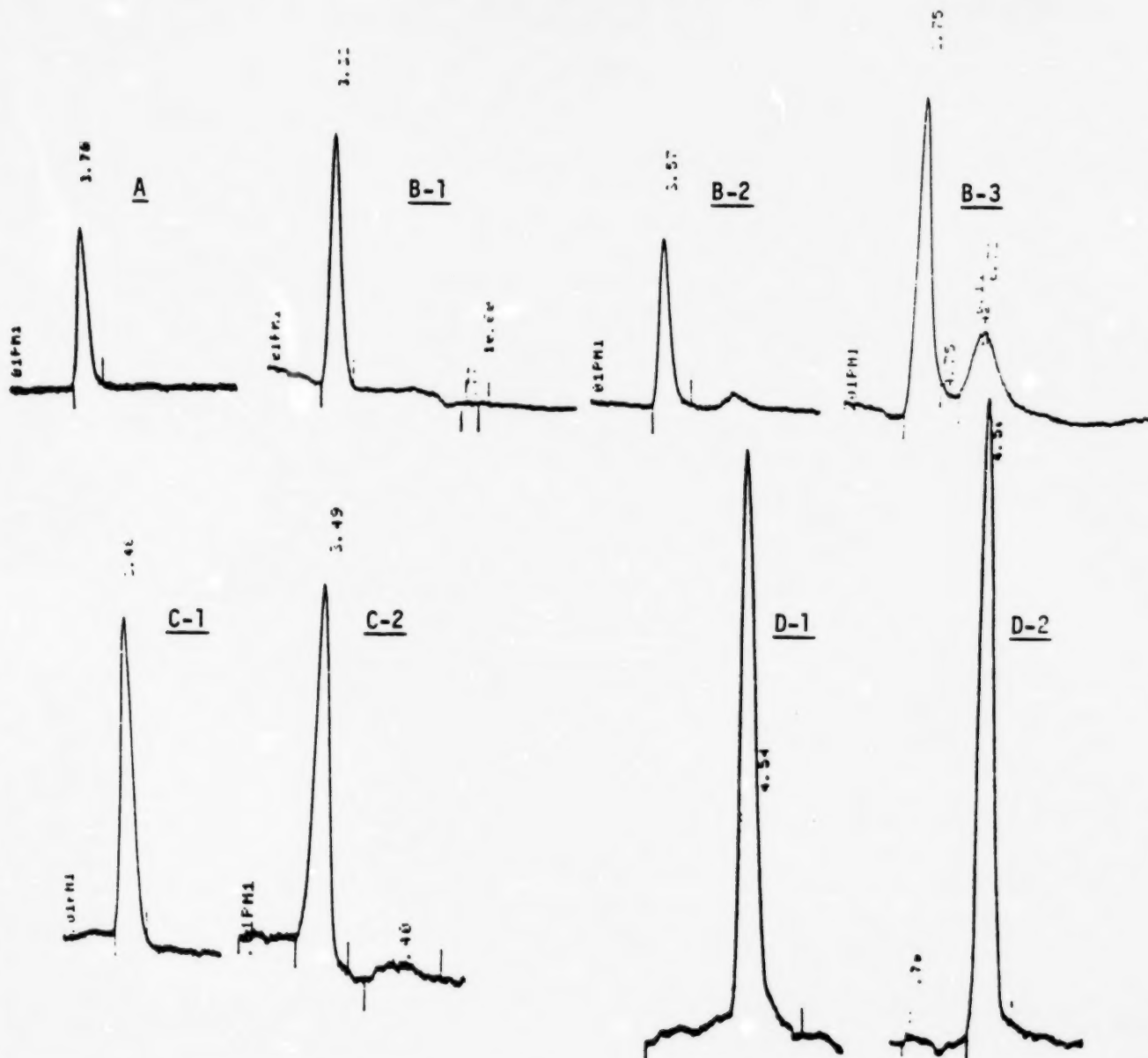


FIGURE 2

Gly-CPG SEHPLC Chromatograms
(Conditions in Table 2)

- A) 4 x 25 cm column; RI detection; 100 ppm Separan MG 700
- B-1) 4 x 25 cm column; UV detection; 10 ppm Separan MG 700
- B-2) 4 x 25 cm column; UV detection; 9.9 ppm Superfloc 127
- B-3) 4 x 25 cm column; UV detection; 9.4 ppm Percol 352
- C-1) 1 x 100 cm column; UV detection; 10 ppm Separan MG 700
- C-2) 1 x 100 cm column; UV detection; 10.7 ppm Superfloc 127
- D-1) 2 x 100 cm column; UV detection; 10 ppm Separan MG 700
- D-2) 2 x 100 cm column; UV detection; 10 ppm Separan MG 700

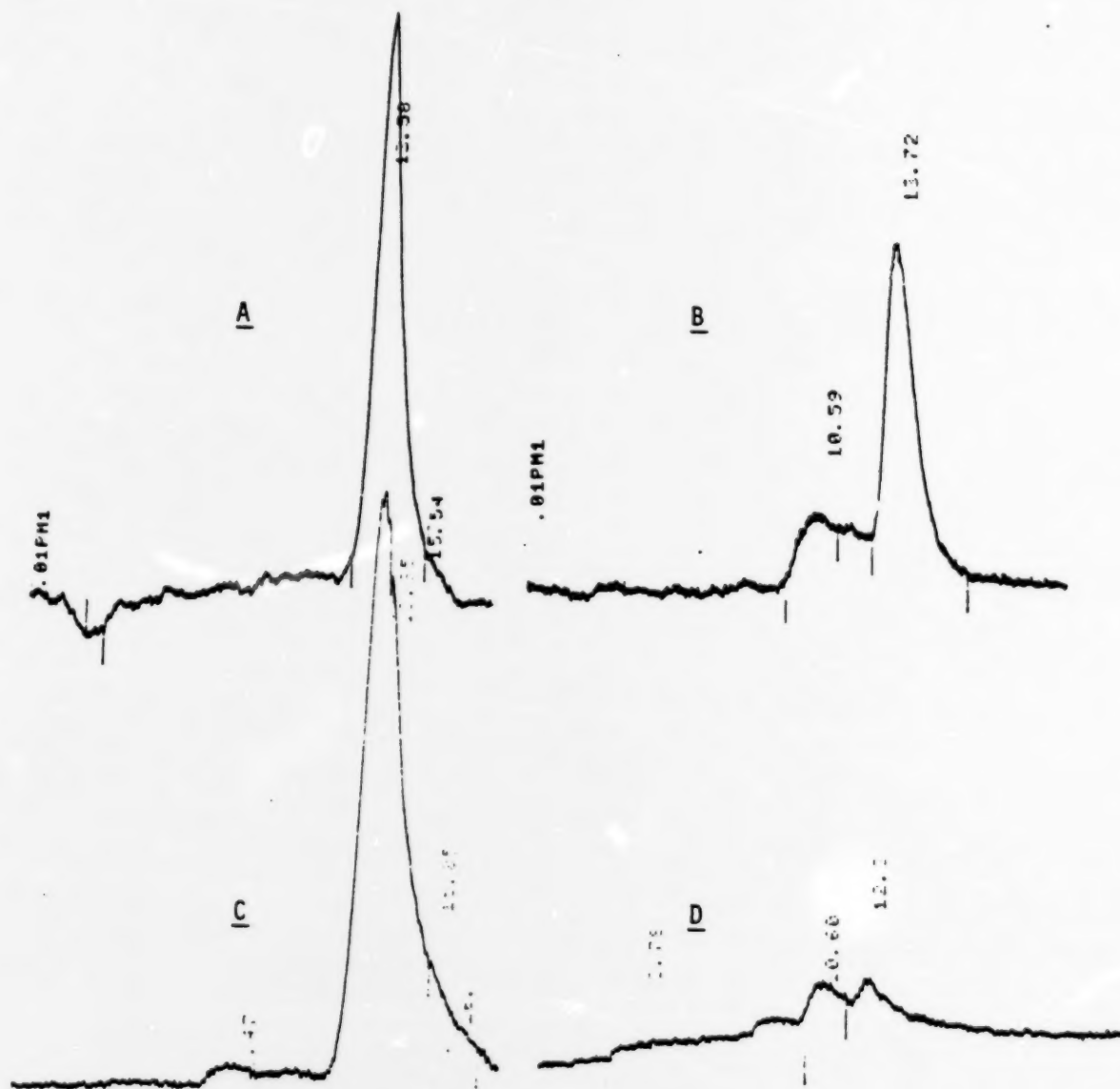
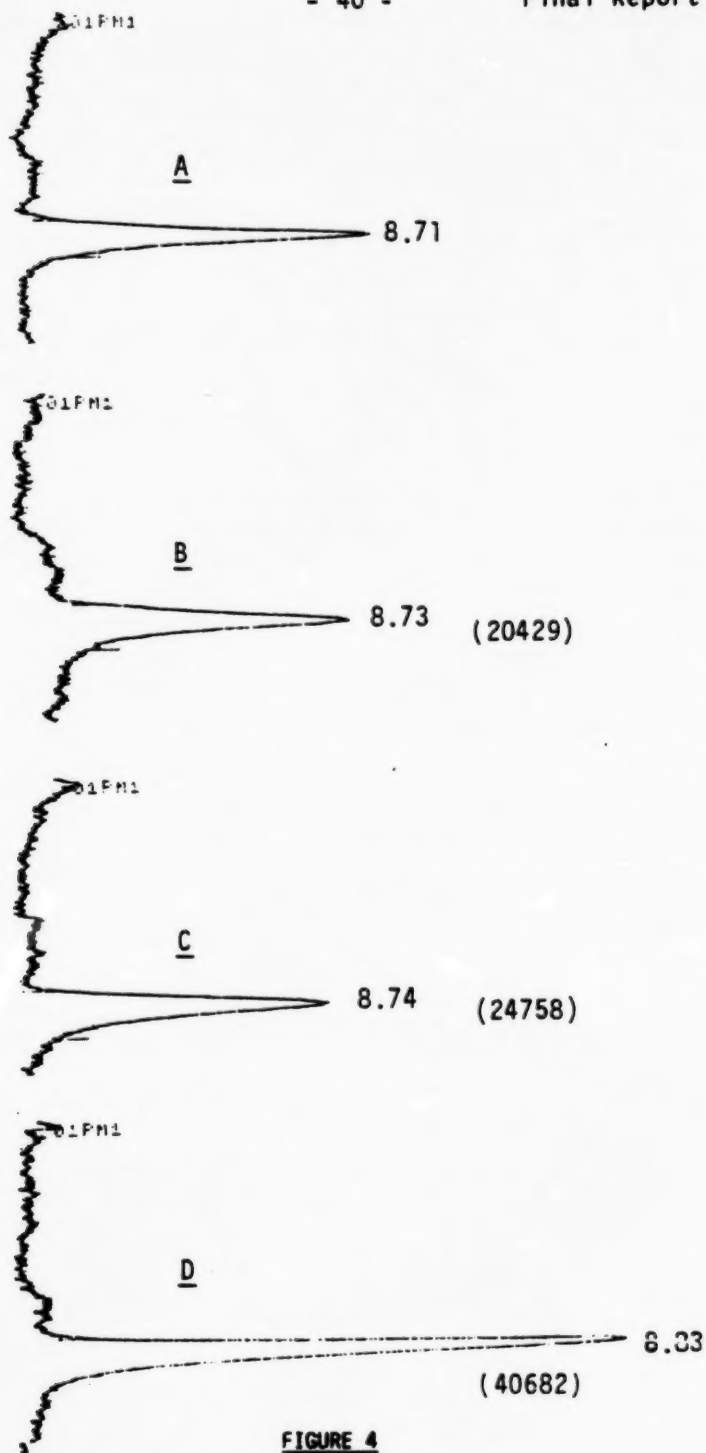


FIGURE 3

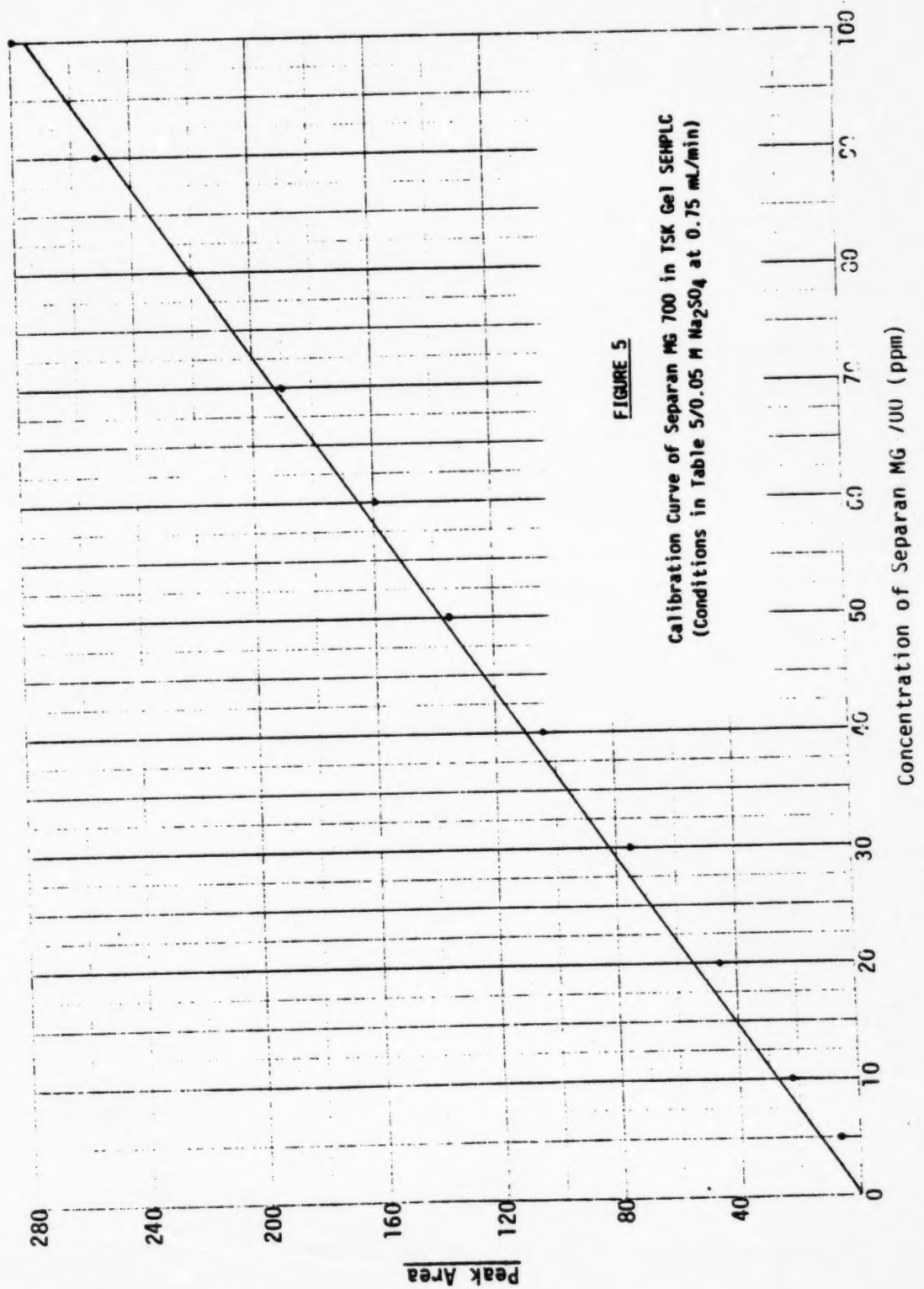
TSK Gel SEHPLC Chromatograms
(Conditions in Table 5/0.05 M NaCl at 0.5 mL/min)

- A) 10 ppm Separan PG 700
- B) 9.8 ppm Superfloc 127
- C) 11.3 ppm Hercofloc 1021
- D) 9.4 ppm Percol 352



TSK Gel SEHPLC Chromatograms
(Conditions in Table 5/0.05 M Na₂SO₄ at 0.75 mL/min)

- A) 10 ppm Separan MG 700
- B) 11.1 ppm Praestol 114 (50% anionic charge)
- C) 10.4 ppm Praestol 2935 (35.4% anionic charge)
- D) 11.6 ppm Praestol 2830 (12.5% anionic charge)



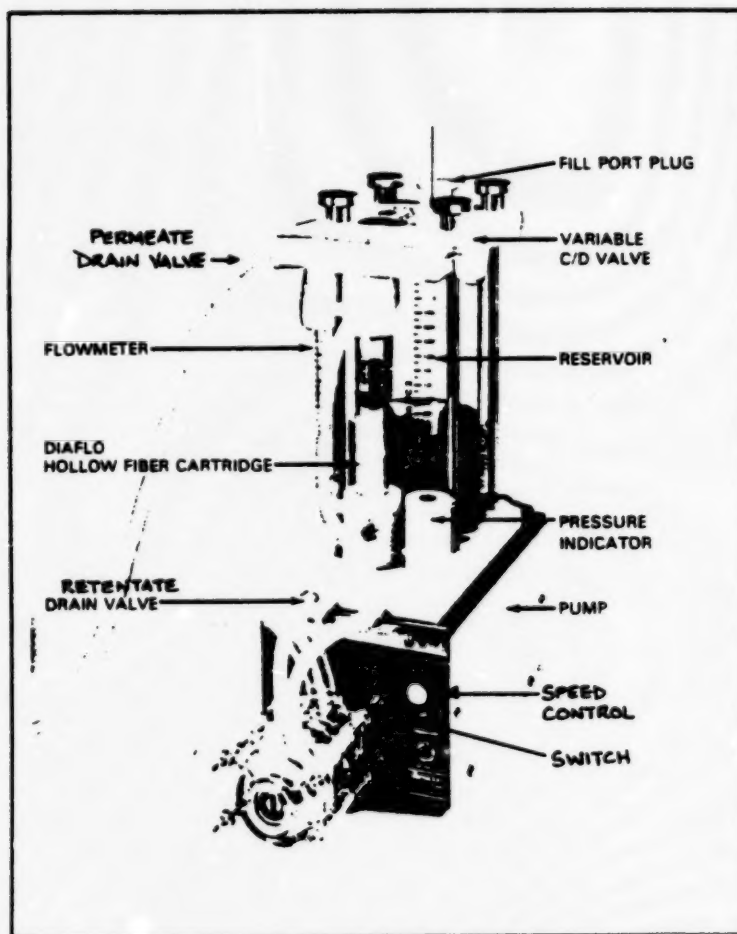


Figure 6—Model DC2, in concentration mode.

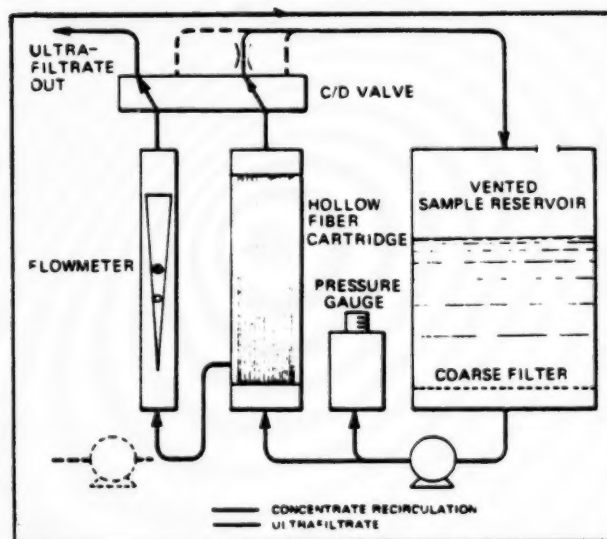


FIGURE 7

Model DC2, Concentration Schematic

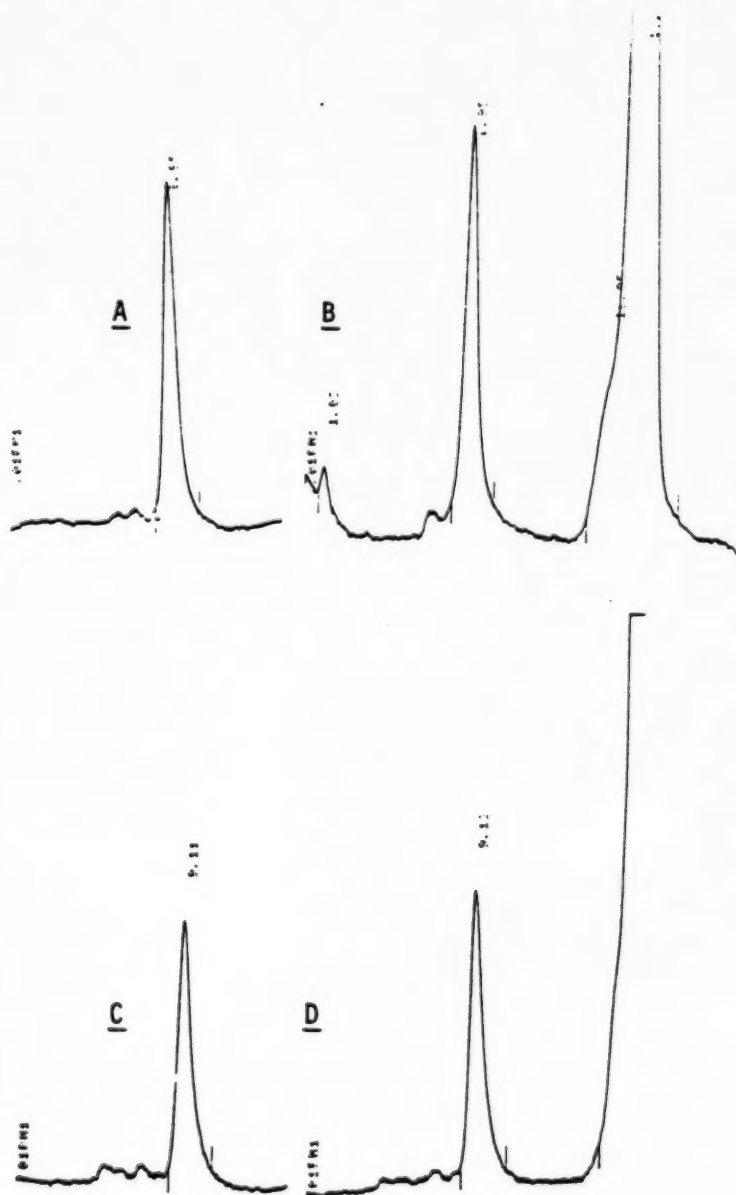


FIGURE 8

Spiking and Recovery Studies with distilled water
(TSK Gel) SEHPLC Conditions in Table 5/0.05 M Na₂SO₄ at 0.75 mL/min

- A) 40 ppm Separan MG 700 standard
- B) Single pass UF retentate of distilled water
spiked at 0.5 ppm level Separan MG 700
- C) 50 ppm Percol E-10 standard
- D) Single pass UF retentate of distilled water spiked at
0.5 ppm level Percol E-10

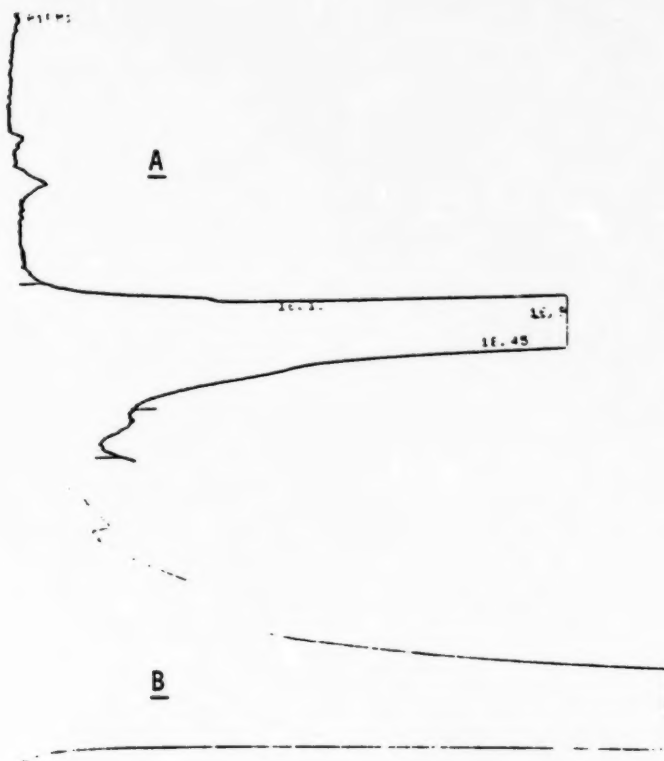


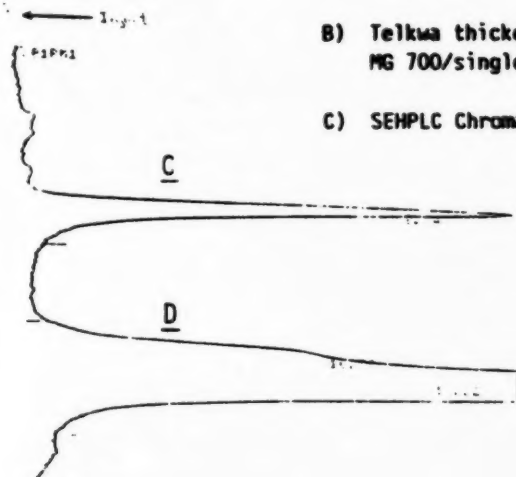
FIGURE 9

Background level and spiking and recovery studies
of Telkwa Coal Washery Thickener Feed filtrate.
(TSK-Gel SEHPLC Conditions in Table 5/0.05 M Na₂SO₄ at 0.75 mL/min)

A) Telkwa thickener feed filtrate/single pass UF/SEHPLC
Chromatogram of UF retentate.

B) Telkwa thickener feed filtrate spiked with 5.0 ppm Separan
MG 700/single pass UF/SEHPLC Chromatogram of UF permeate.

C) SEHPLC Chromatogram of UF retentate of B)



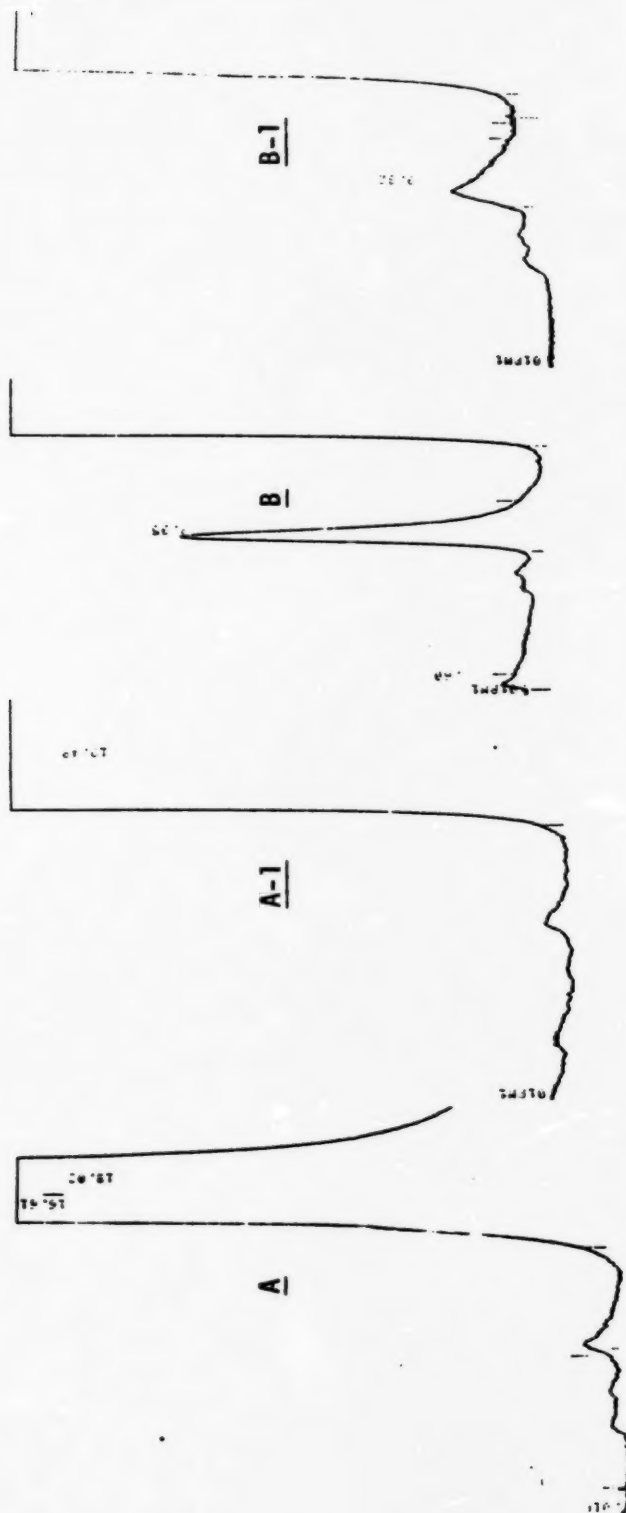


FIGURE 10

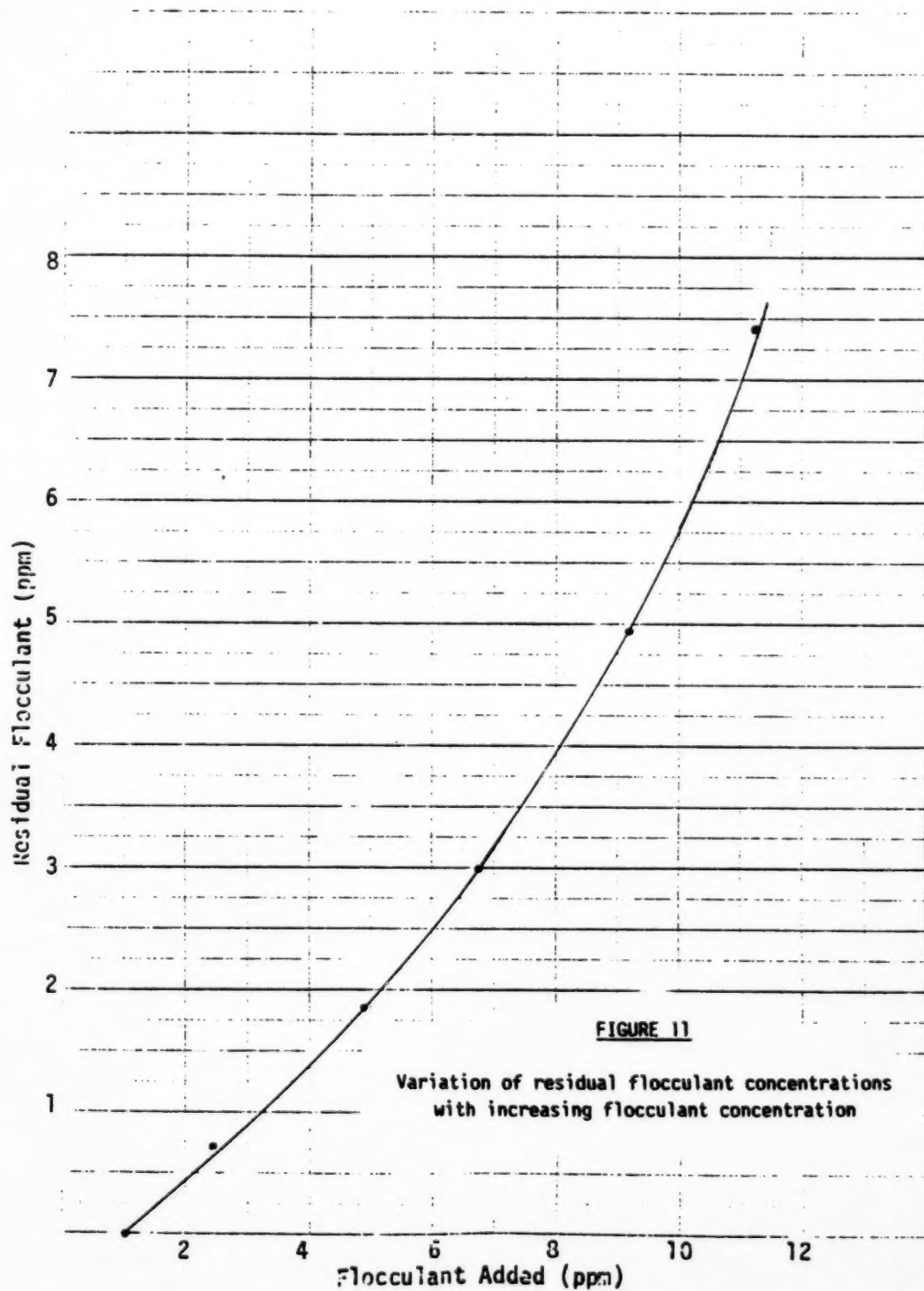
TSK Gel SEHPLC Chromatograms of UF retentates and permeates.
(SEHPLC Conditions in Table 5/0.05 M Na_2SO_4 at 0.75 mL/min)

A) Telkwa thickener feed - flocculation with 2.44 ppm
Separan MG 700/filtered and single pass UF/UF retentate.

A-1) UF permeate of A).

B) Telkwa thickener feed - flocculation with 7.41 ppm
Separan MG 700/filtered and single pass UF/UF retentate.

B-1) UF permeate of B).



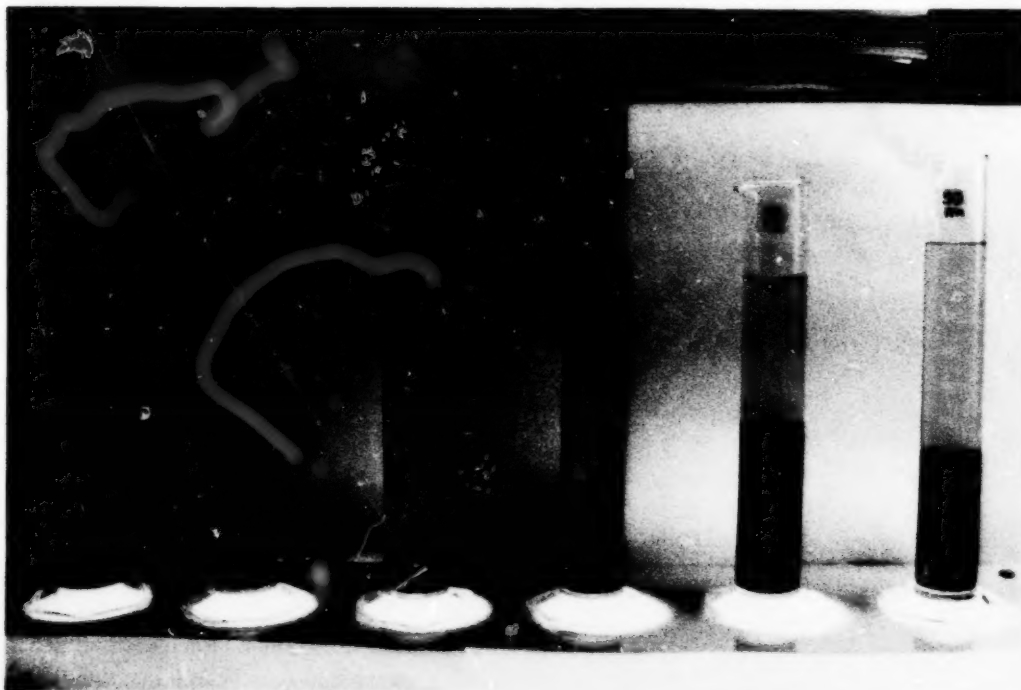


FIGURE 12

Photograph showing flocculation of Tar Sands Tailings Emulsion

APPENDIX

Spectrophotometric Determination of Polyacrylamide (PAM)
in Water

- Method of determining concentration of PAM
in UV range at $\lambda 287$ nm
- A new method of determining concentration of
PAM employing Leuco Crystal Violet in the
visible range, $\lambda 582$ nm

by

Raj N. Pandey

Raj N. Pandey, Ph.D.

I.0 SPECTROPHOTOMETRIC METHOD

I.1 Introduction

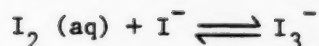
Previous section described the SEHPLC technique for the determination of PAM in aqueous solution, which is used as flocculant in treatment of coal and oil processed water. A simple, economical and routinely applicable method is required which can be used in ordinary course of laboratory set-up. One such method is spectrophotometric method, adapted by the Dow Chemical Company (1) in distilled water in the UV range of the spectrum. To confirm the suitability of this method for the measurement of PAM in coal and oil process waters studies of spectrophotometric method development were undertaken. The method development study covered the UV as well as the visible range of the spectrum. A new method was developed employing Leuco Crystal Violet to measure the absorbance at $\lambda 592$ nm. This latter method is considered to be superior to the UV method since most of the interferences of the materials present in the process water can be avoided. Leuco crystal violet is inexpensive and is available from the Aldrich Chemical Company in a very pure form that readily dissolves in acidified water.

II.0 Analytical Technique

II.1 UV Method

The NH_2 groups of the Polyacrylamide (PAM) polymer was brominated by addition of bromine water to N-bromoamide (PAM-Br). The excess bromine was destroyed by addition of a solution of sodium formate. The N-bromo amide oxidizes iodide ion to Iodine. When an excess of iodide ion is present, the tri-iodide ion is formed, since iodine is

(1) The Dow Chemical Company, Midland, Michigan 48640, Report ML-AM73-25, 1973



readily soluble in a solution of iodide. The concentration of tri-iodide is thus related to PAM concentration. The distinctive absorbance of tri-iodide at λ_{287} nm was used to measure PAM concentration.

II.2 Interferences

The interferences (Intf.) from the possible materials present in water in the UV region of the spectrum could be:

- Dissolved organics e.g. bitumen acid, humic/fulvic acid etc...
- Dissolved inorganic ions
- Other amide groups containing materials
- Any impurities that react with bromine and brominated product absorbing at these wavelengths

Most of the above interferences (intf) can be corrected using untreated (PAM-free) water from the same source as a reference solution.

For solutions at a particular wavelength (287 nm in this study), where the species of PAM and PAM-Br do not contribute significantly to the optical density and which differ only in that one (S=Sample) contains tri-iodide ion and the other (R=Reference) does not, the difference in optical densities of the two solutions is given by:

$$\Delta D = D_S - D_R$$

$$\text{Where } D_S = D_{PAM} + D_{PAM-Br} + D_{Intf} + D_{Reagent} + D_{I^-} + D_{I_3^-}$$

$$D_R = D_{Intf} + D_{Reagent} + D_{I^-}$$

At $\lambda 287$ nm the contribution to optical density due to PAM and N-bromo PAM is negligibly small. i.e.

$$D_{\text{PAM}} + D_{\text{PAM-Br}} \longrightarrow 0$$

$$\Delta D = D_S - D_R = D_{I_3^-} = K[\text{PAM}], \text{ where } K \text{ is constant}$$

Thus a plot of ΔD vs $[\text{PAM}]$ should be linear. Small absorbances due to species of PAM and PAM-Br in sample solutions would be expected to put greater weightage in the low concentration range of PAM in the plot of ΔD vs $[\text{PAM}]$.

II.3 Experimental Approach

II.3.1 Apparatus

Beckman Acta III dual beam spectrophotometer equipped with chart recorder and digital read-out were used. Precisely matched 5 cm quartz cells were used to measure absorbance at $\lambda 287$ nm.

II.3.2 Materials

Acetate buffer (pH = 5.5), saturated bromine water, sodium formate solution, 5g in 100 ml water and potassium iodide solutions, 15 g in 100 ml of water, were prepared from ACS reagent grade materials obtained from BDH Chemical Company.

The polyacrylamide (PAM) solution was prepared from Separan MG 700 from the Dow Chemical Company. To an accurately weighed 70-80 mg of PAM, 1 ml of distilled in glass methanol was added to wet the polymer. The flask was partially filled with distilled water and the solution was stirred for five hours prior to final volume make-up. Two stock solutions were prepared and appropriate dilutions made in the measurement of spectrophotometric data.

II.3.3 Procedure

A series of PAM standards were prepared. To each standard sufficient distilled water was added to maintain a constant volume of 25 ml. A known quantity of buffer solution and bromine water were added, mixed and allowed 10 minutes for the reaction. Excess bromine, as indicated by the colour was destroyed by sodium formate solution. A known volume, 110 ml of potassium iodide solution was added, mixed and measurement of absorbance were made at 287 nm within five minutes. The reference solution contained distilled water with all the reagents except PAM. A calibration plot of absorbance vs concentration of PAM was made from which the concentration of PAM in the sample water was calculated. As shown in the result section the plot of ΔD vs Concentration of PAM is linear.

II.3.4 Calibration Curves

Using the above procedure (II.3.3) the absorbance of a series of solution containing varying amounts of PAM (2 to 56.6 ug in 37.2 ml solution) were measured. The results are given in table II.1 and the data plotted in figure II.1.

Table II.1

The absorbance of triiodide complex at λ_{287} nm, pathlength of 5 cm at varying concentrations of PAM.

Run #	PAM Used DOW Separan MG 700 (ug)	PAM * ppm	D_S λ_{287} nm
1	56.664	1.52	0.417
2	42.498	1.14	0.314
3	41.352	1.11	0.745
4	33.998	0.91	0.297
5	27.568	0.74	0.248
6	13.784	0.37	0.207
7	5.666	0.15	0.135
8	2.757	0.07	0.141
Blank	-----	-----	0.124

* Concentration in solution

II.4 Pam Spiking and Recovery

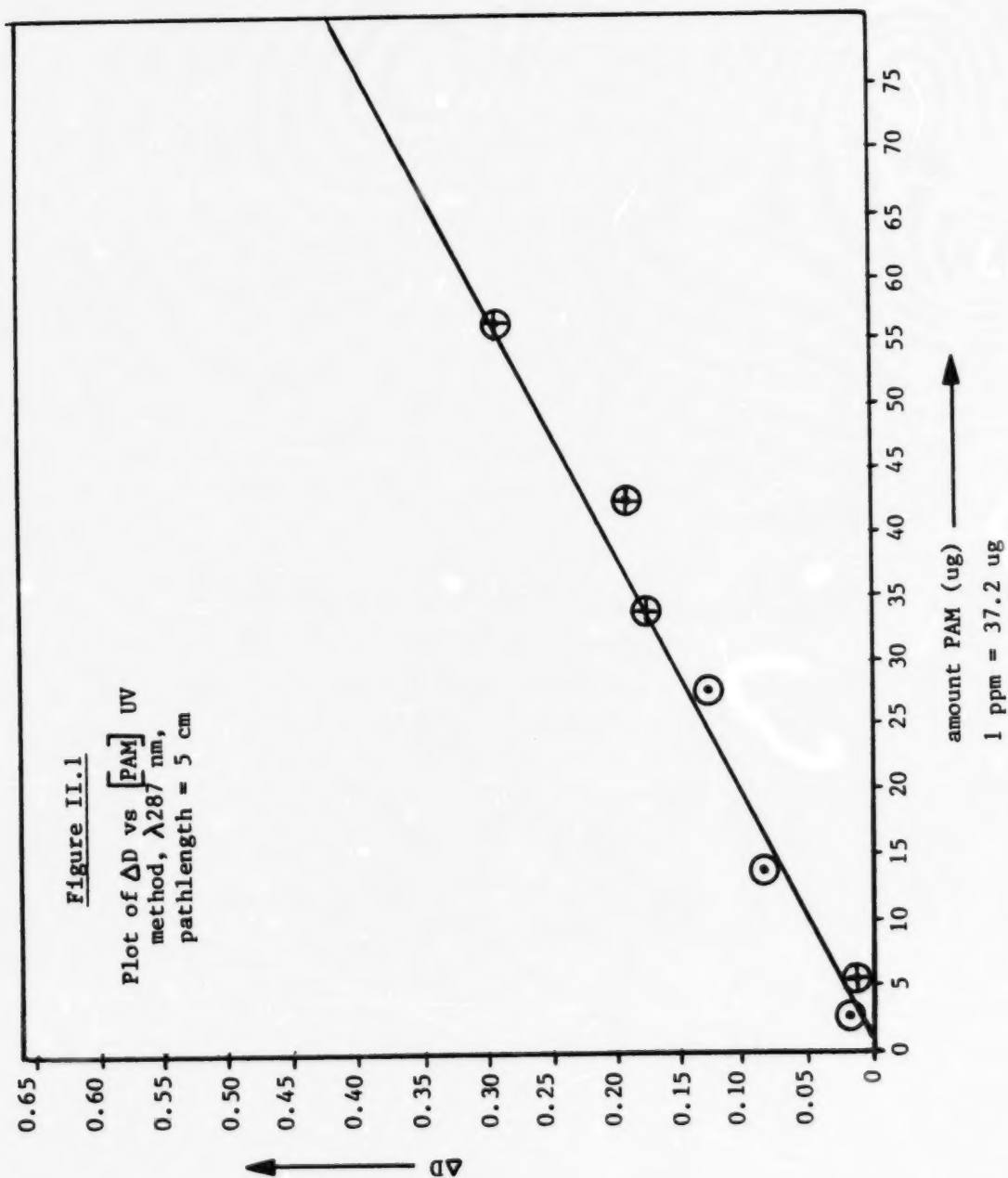
Spiked samples prepared from Ontario Research Foundation Laboratories were analyzed for PAM concentration. The analysis was delayed by three months due to Leuco Crystal Violet method development studies in progress. The first set of analysis performed were in error due to unmatching cells. The analysis of four samples where sufficient sample volume was available are presented in table II.2.

Table II.2

Result of Analysis of Spiked Samples Using UV Method

ORF Sample #	Absorbance* at λ_{287} nm	PAM found ppm
40 ppm	0.196	36.84
35 ppm	0.144	27.07
30 ppm (16508)	0.185	34.77

*Corrected for Blank



III.0 Leuco Crystal Violet Method

III.1 Principle of the Method

A new method was developed for determining trace amounts of PAM in water by a combination of UV method (II.1) and Leuco Crystal Violet method used in trace determination of Iodine in water and waste water.

In this method, iodide is oxidized to iodine by N-bromo amide polymer (PAM-Br) produced by bromination of PAM. The iodine that is produced reacts instantaneously with colourless Leuco Crystal violet, 4,4',4''-methylidynetris (N,N-dimethylaniline) to produce intense blue colour. The developed colour is stable and obeys Beer's law over range of PAM concentration in excess of iodide ion.

Several difficulties were encountered in the development of this method:

- The bromination reaction proceeds at pH = 5.5
- The Leuco Crystal Violet reaction is optimum in the pH range of 3.6 to 4.3
- Iodide ion concentration must be in excess

The method described below is found to yield satisfactory results.

III.2 Interferences

The interferences (Intf.) for possible materials present in water (see II.2) will be minimum, if any, in the visible spectrum at $\lambda 592$ nm. Since PAM, PAM-Br, reagents used in the method do not absorb, it can be readily shown that the difference in optical densities of sample (S) and reference (R) is given by

$$\Delta D = (D_S - D_R) = D_{I_2\text{-Leuco}} = K [PAM]$$

where $D_{I_2\text{-Leuco}}$ = Absorbance due to Leuco Crystal Violet complex.

Thus a plot of ΔD vs concentration of PAM should be linear.

III.3 Experimental Approach

III.3.1 Apparatus

The absorbance at $\lambda 592$ nm was measured using precisely matched 5 cm cells Beckman Acta III dual beam spectrophotometer.

III.3.2 Materials

Acetate buffer, saturated bromine water, sodium formate solution, potassium iodide and polyacrylamide (PAM) solutions were prepared as before (II.3.2). In addition the following solutions were prepared from analytical reagent grade materials obtained from BDH Chemical Company, citric buffer, pH = 3.8 by mixing appropriate concentrations of citric acid and ammonium hydroxide solution.

Leuco Crystal Violet indicator was prepared by dissolving 1.5 g of 4,4',4'' - methylidynetris (N,N - dimethylaniline, Aldrich Chemicals) in 200 ml of water and 3 ml of concentrated H_2SO_4 was added. The solution was stirred with magnetic stirrer bars until dissolved. To 800 ml of water was added 2.5 g of $HgCl_2$ and the solution was stirred until dissolved. The leuco crystal violet and $HgCl_2$ solutions were mixed and the pH was adjusted to 1.5 by adding H_2SO_4 dropwise. The solution was stored in brown glass bottle with a glass stopper.

III.3.3 Procedure

A suitable portion of stock PAM solution was diluted in series of increments in the flask, and the volume made up to 25 ml. 10 ml of acetate buffer, pH = 5.5 was added. To this solution was added 1ml of saturated bromine water. The solution was mixed and let stand for 10 minutes. At this stage 0.2 ml of sodium formate solution was added to destroy excess bromine. After performing the bromination steps, 1 ml of 5000 ppm potassium iodide solution was

added and the pH was lowered to 4.0 by dropwise addition of dilute H_2SO_4 (2.80 ml conc. H_2SO_4 diluted to 50 ml). To this solution, 10 ml of citric buffer was added followed by addition of 1.0 ml of leuco/ $HgCl_2$ solution. The solution was shaken to mix. The coloured standards of known PAM concentration were transferred to cell of 5 cm pathlength and read the absorbance in a spectrophotometer at a wavelength of 592 nm against distilled water. Absorbance was measured within 5 minutes after adding the leuco crystal violet indicator solution. The reference solution was prepared in the same manner except that no PAM was added. As shown in the result section the plot of absorbance vs concentration of PAM is linear.

III.3.4 Calibration Curves

Using the above procedure (III.3.3) the absorbances of a series of solutions containing varying amounts of PAM (35 ug to 700 ug) were measured at $\lambda 592$ nm. The results are given in table III.1 and data plotted in Figure III.1.

Table III.1

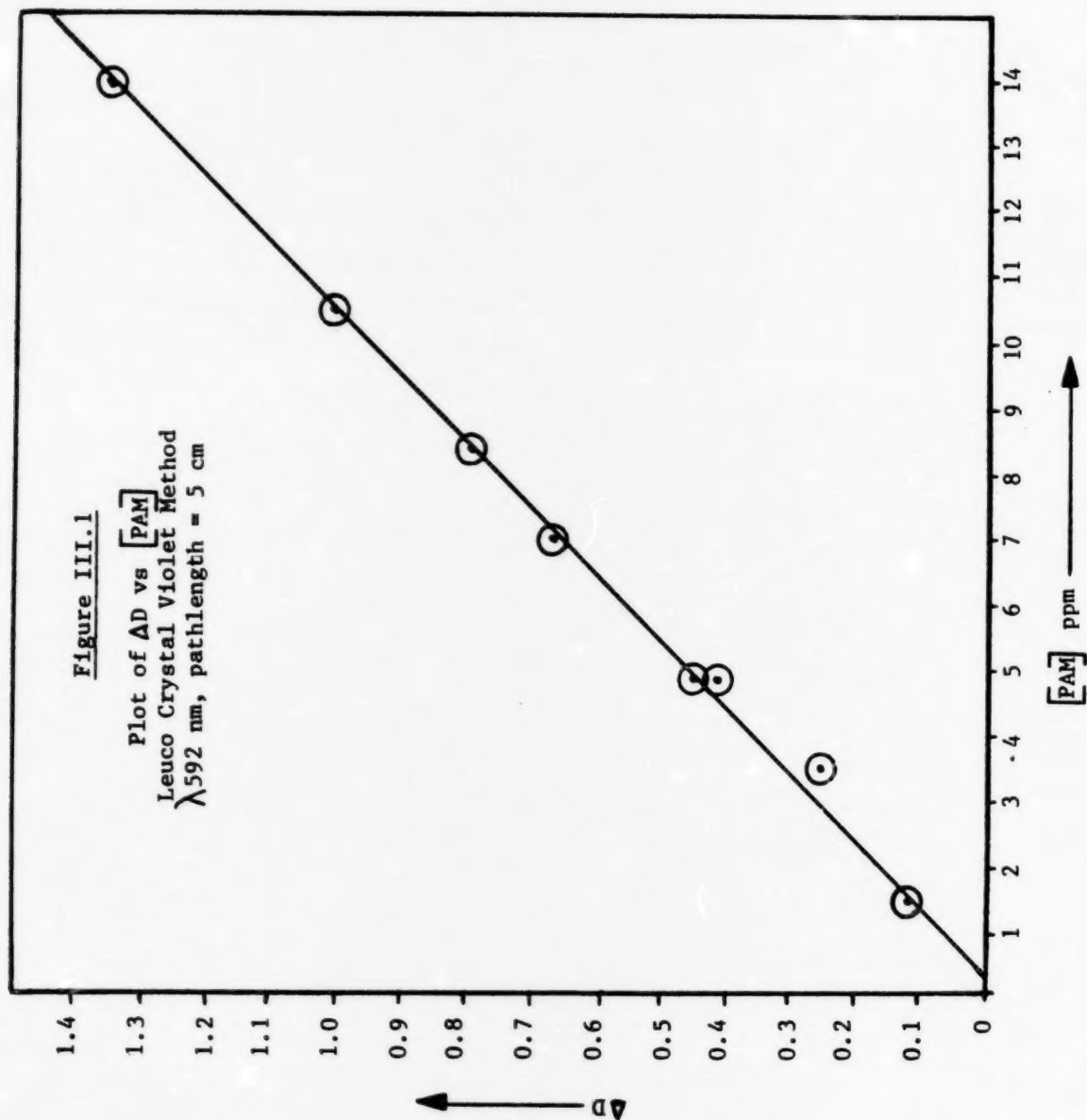
The absorbance of Leuco Crystal Violet complex at $\lambda 592$ nm, pathlength of 5 cm at varying concentrations of PAM.

Run #	PAM used - DOW Separan MG 700 (ug)	[PAM] ppm	D_S^* $\lambda 592$ nm
1	70.16	1.396	0.118
2	175.40	3.494	0.265
3	245.60	4.886	0.426
4	350.80	6.998	0.682
5	420.96	8.385	0.816
6	526.20	10.482	1.061
7	701.60	13.976	1.368
Blank	-	-	0.016

* absorbance of samples

Figure III.1

Plot of ΔD vs $[PAM]$
Leuco Crystal Violet Method
 λ 592 nm, pathlength = 5 cm



III.4 PAM Spiking and Recovery in Sample of Tar Sands Tailings

An untreated sample of tar sands tailings composed of bitumen-water-suspended fines O/W emulsion was supplied by Suncor Inc. The sample's pH, % suspended fines and % bitumen were analysed at Ontario Research Foundation and have been reported earlier on page 7 of this report. The supernatant removed by decantations was filtered twice with Whatman filter paper. The filtrate was analysed for Na, K, Ca and Mg metals by standard atomic absorption spectrophotometry and following results were obtained:

Table III.2

Metal	Concentration ppm
Na	8.88
K	9.32
Ca	4.11
Mg	2.22

Preliminary spiking and recovery studies were performed with raw filtrate sample. The type of PAM used for spiking was separan MG700, at high concentration range. A calibration curve was prepared using distilled water. From the measured absorbance the quantity of PAM recovered was calculated.

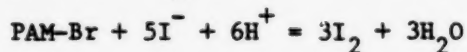
Table III.3

Recovery of Saparan MG700 in Tar Sand

PAM spiked ug	PAM recovered ug
525.5	503.2
350.4	363.3
175.2	185.6

III.5 Other Attempted Methods

The following alternative procedure was tried. This method is based on titration or spectral measurement involving iodine. As in previous methods, I_2 was produced in solution.



A solution of iodine in aqueous iodide has an intense yellow to brown colour. The test was made by use of a solution of starch as an indicator. Starch reacts with iodine in the presence of iodide to form an intensely blue-coloured complex, which is visible at very low concentrations of iodine.

This property of intense blue colour was attempted for the determination of low concentration of PAM. The method of simple titrimetry was used employing standard solution of sodium thiosulfate. However, the volume of sodium thiosulfate required was too small to yield reliable results. Alternatively the spectrophotometric method was attempted but the turbidity due to starch solution resulted in an inaccurate result.

III.6 Recommendations for Future Work

The remarkable feature of the spectrophotometric method development study has been noted in terms of :

- Simplicity
- Economical
- Routinely applicable in the field
or laboratory

In view of the development of new promising method employing Leuco Crystal Violet, this study should be continued. A combined method of ultrafiltration and spectrophotometry should be further developed and applied to the analysis of polyacrylamide in the low as well as high concentration range of PAM. The studies should be expanded to cover coal washery effluents, tar sand tailings, industrial waste water and refinery oil waste water. The objective of this study would be to develop economical method that becomes routinely applicable to industrial users.